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Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance

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METALS IN SOIL (FIELD SCREENING)—EDXRF

Analtyes: Metals (K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, Sb, Ba, Hg, Pb, U, Th)	**Method No.:** EI732
Matrix: Soil or geological samples	**Accuracy and Precision:** For >1000 ppm, accuracy = 93-109%, precision (1σ) = 2-13% . For 20-1000 ppm, accuracy = 70-109%, precision (1σ) = 8-35%.
Procedure: Energy-dispersive x-ray fluorescence spectrometry	**Minimum Detectable Concentration:** ~10 ppm
Effective Date: 09/01/93	**Author:** Steve Goldstein

SAFETY NOTE: Before beginning this procedure, read SOP-17 of the Environmental Chemistry Safety Manual. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.5 for proper waste disposal practices.

1. Principle of Method

1.1. Soil samples are dried, powdered, and sieved.

1.2. Samples are analyzed for trace metals by energy-dispersive x-ray fluorescence spectrometry (EDXRF).

2. Sensitivity

2.1. Sensitivity is determined by the counter background, excitation, and detection efficiency.

2.2. For routine measurements with a 200-s live time for each excitation condition, the minimum detection limit (signal above 3 σ of the background) is approximately 10 ppm.

3. Accuracy and Precision

3.1. Concentration range, average accuracy, and replicate precision (1 σ) for four soil standards (10 analytes) are summarized below:

K (1-5%)	= 93 ± 2%
Ca (1-20%)	= 109 ± 13%

Ti (0.1-1%)	=	98	±	3%
Cr (10-200 ppm)	=	83	±	8%
Mn (200-1000 ppm)	=	109	±	16%
Fe (1-10%)	=	105	±	3%
Cu (10-100 ppm)	=	93	±	28%
Zn (10-200 ppm)	=	70	±	35%
Ba (100-1000 ppm)	=	99	±	8%
Pb (10-100 ppm)	=	95	±	16%

4. Interferences

4.1. Spectral overlaps are automatically corrected by the data analysis program. Small amounts of As in the presence of large amounts of Pb, however, appear to be difficult to resolve.

5. Collection and Storage of Samples

5.1. Soil samples are collected in polybottles. A 10-g sample is required for analysis. There are no special storage requirements.

6. Apparatus

6.1. XRF Spectrometer: Spectrace 6000 EDXRF spectrometer, equipped with x-ray tube excitation, electrically cooled SiLi detector, and IBM-compatible 386 computer for system operation, spectral processing, analysis, and storage.

6.2. Microwave: Sears Kenmore micro\convection oven #89561.

6.3. Mixer/mill: Spex 8000 mixer mill.

6.4. Grinding vials: Spex #8005 zirconia ceramic vial set.

6.5. Sieves: 100- and 10-mesh, nylon screen with plastic frame, 70-mm-diam, Spex #3536.

6.6. XRF sample cups: disposable, polyethylene, 31-mm-diam, Chemplex #1430.

6.7. X-ray film: Prolene, 0.00016-in. gauge, Chemplex #416.

6.8. Petri dish: Pyrex, 94-mm-diam.

6.9. Weighing paper: VWR #12578-165.

7. Reagents

7.1. No reagents are required.

8. Calibration and Standards

8.1. Calibration of the EDXRF spectrometer.

8.1.1. Energy calibration of the spectrometer is performed daily using the copper K-alpha line. Stability and resolution are checked on a monthly basis, with the following specifications for copper:

Full-width half maximum (FWHM): <220 ev ± 5 ev maximum
Peak centroid: 8041 ± 3 ev maximum
Total counts: 2 million or more ± 0.5% maximum
Peak counts: 1 million or more ± 0.5% maximum
Elapsed time: 8 h

8.2. Pure-element standards.

8.2.1. Reference spectra are acquired for each analyte as well as major or minor components that have interfering x-ray lines. Pure-element metals or compounds are used to acquire these spectra.

8.3. Soil standards.

8.3.1. Peak intensities are converted to concentrations using a fundamental parameters analysis method, with five soil standards used to determine pure-element count rates. Standards and samples are analyzed under identical conditions.

8.3.2. The following Standard Reference Materials (SRMs) are used for calibration: National Bureau of Standards (NBS) SRM 2704, NBS SRM 1648, NBS SRM 1646, Canadian Certified Reference Material (CCRM) SY-2, and CCRM BL-4.

8.3.3. For quality control (QC) purposes, at least one standard per 10 samples should be analyzed as an unknown.

8.4. Open and blind QC standards.

8.4.1. One each of open and blind QC soil or geological standards should be analyzed per 10 samples. One uncontaminated background sample should also be analyzed per 10 samples.

9. Procedure

9.1. Sample preparation.

9.1.1. Shake the sample container and transfer approximately 20 g of sample into a petri dish.

9.1.2. Microwave on 50% power for 5 min or until dry.

9.1.3. Pass the sample through a <10-mesh screen to remove large objects, then pass <10-mesh sample through a 100-mesh screen. Discard the >10-mesh fraction.

9.1.4. Transfer the >100-mesh fraction to a zirconia vial. Mill/mix the sample for 5 min.

9.1.5. Pass the milled sample through a 100-mesh screen.

9.1.6. Transfer the <100-mesh sample to an XRF sample cup. Fill the sample cup to the top with sample.

9.1.7. Cover the sample cup with prolene film, and label it with the request and sample number.

9.1.8. Between samples, clean the equipment with a dry Kimwipe. At the end of preparation, rinse the equipment with water.

9.2. Sample analyses.

9.2.1. Samples are analyzed under the following conditions:

Low Z (K-Fe lines):
- 0.127-mm Al filter
- tube voltage = 13 kV
- tube current = 0.35 mA
- live time = 200 s.

Mid Z (Ni-Se K lines, Hg-U L lines):
- 0.127-mm Al + 0.127-mm Rh filter
- tube voltage = 30 kV
- tube current = 0.30 mA
- live time = 200 s.

High Z (Cd-Ba K lines):
- 0.127-mm Al + 0.63-mm Cu filter
- tube voltage = 50 kV

- tube current = 0.35 mA
- live time = 200 s.

9.2.2. Open and blind QCs, standards, and duplicate samples are analyzed at a frequency of 10%.

10. Operation of the X-Ray Fluorescence Spectrometer

10.1. Refer to the operating manual for the XRF spectrometer.

11. Calculations

11.1. Total peak and background counts are determined for each analyte. Net counts are converted to concentration by use of a fundamental parameters (FP) program, using five standards to determine pure-element count rates for each analyte. The FP program corrects for any matrix enhancement or absorption effects.

11.2. Calculations are made using the following formulas.

11.2.1. Detection limit.

$$C_{LLD} = \frac{3 \times C_{Std} \times \sqrt{N_b}}{N_n} ,$$

where C_{LLd} = detection limit,
C_{Std} = concentration of analyte in the standard,
N_b = total background counts, and
N_n = net peak counts.

For a 200-s live time, typical detection limits are approximately 10 ppm.

11.2.2. Precision due to counting statistics.

$$\%RSD = \frac{\sqrt{N_g + N_b}}{N_g - N_b} \times 100\% ,$$

where %RSD = percent relative standard deviation,
N_g = gross counts, and
N_b = background counts.

The precision calculation is due to counting statistics only and is only one source of variance in the measurement. Other contributors to variance include instrumental precision, sample preparation, and sampling. Analysis of replicates is a more reliable but tedious way to determine overall precision.

12. Proper Waste Disposal Practices

12.1. Soil samples are returned to the Sample Management section for disposal.

13. Source Materials

13.1. W. Watson, J.P. Walsh, and B. Glynn, "On-Site X-Ray Fluorescence Spectrometry Mapping of Metal Contaminants in Soils at Superfund Sites," *American Laboratory* (1989).

13.2. D. E. Leyden, "Energy-Dispersive X-Ray Spectrometry," *Spectroscopy* 2, 28-36 (1987).

13.3. A. R. Harding, "Fundamental Parameter Method EDXRF Analysis of Contaminated Soils," *Spectrace Technical Review.*

13.4. Spectrace 6000 Operators, Technical, and Software Manuals.

13.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

13.6. "Handling and Disposal of Hazardous Materials," SOP-3, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Appendix III, Los Alamos National Laboratory document (most recent edition).

13.7. "Operation of an Energy-Dispersive X-Ray Fluorescence Spectrometer," SOP-17, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Appendix III, Los Alamos National Laboratory document (most recent edition).

13.8. National Bureau of Standards, "Standard Reference Material 1646, Estuarine Sediment" (National Bureau of Standards, Washington, DC, June 7, 1982).

13.9. National Bureau of Standards, "Standard Reference Material 1648, Urban Particulate Matter" (National Bureau of Standards, Washington, DC, May 11, 1982).

13.10. National Bureau of Standards, "Standard Reference Material 2704, Buffalo River Sediment" (National Bureau of Standards, Gaithersburg, MD, June 1, 1988).

13.11. J. C. Ingles, R. Sutarno, W. S. Bowman, and G. H. Faye, "Radioactive Ores DH-1, DL-1, BL-1, BL-2, BL-3, and BL-4—Certified Reference Materials," Canada Centre for Mineral and Energy Technology report 77-64 (1977).

13.12. Sydney Abbey, A. H. Gillieson, and Guy Perrault, "SY-2, SY-3 and MRG-1: A Report on the Collaborative Analysis of Three Canadian Rock Samples for Use as Certified Reference Materials," Canada Centre for Mineral and Energy Technology report MRP/MSL 75-132 (TR) (1975).

VOLATILE ORGANIC COMPOUNDS: THERMAL DESORPTION OF AIR SAMPLING TUBES—GCMS

Analyte: See Table I at end of procedure	**Method No.:** EO700
Matrix: Sampling tubes	**Detection Limits:** See Table I
Procedure: Desorption and gas chromatography–mass spectrometry	
Effective Date: 04/01/93	**Author:** Anthony Lombardo

SAFETY NOTE: Before beginning this procedure, read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 11 of this procedure for proper waste disposal practices.

1. Principle of Method

Samples are taken by passing a known volume of gas-phase sample through a sample tube containing adsorbent materials. Organic sample constituents are adsorbed onto the adsorbent. The tube is heated while passing an inert gas through the tube. This process desorbs the organic sample constituents off the adsorbent. The inert gas stream is directed to the head of a gas chromatograph (GC) column followed by gas chromatography–mass spectrometry (GCMS) analysis. The sample gas stream may be split before loading onto the GC column.

2. Interferences

Matrix interferences are not usually a problem because the adsorbents capture organic constituents. Moisture is sometimes a problem on high-humidity samples. The purge-and-trap concentrator presently in use has a moisture control module that minimizes this problem. Compounds that coelute and whose spectra generate similar ions may cause interference.

3. Apparatus

3.1. Sample tubes: glass, 5-mm-i.d. × 9-cm-length, containing 150 mg each of 20/40 carbotrap c, 20/40 carbotrap b, and 60/80 carbosieve SIII (custom-made by Supelco, Inc.).

3.2. Culture tubes with Teflon-lined screw caps, to hold sample tubes.

3.3. Friction-seal paint cans.

3.4. Activated charcoal.

3.5. Zipper-lock bags.

3.6. Syringes: gas-tight, removable needle, ranging in volume from 0.5 mL to 50 mL for gas-phase standards. Gas-tight, fixed needle, from 10 μL to 500 μL for liquid standards.

3.7. Syringe needles, side port.

3.8. Gas bulbs: glass, 2.0-L to 500-mL, with septa ports.

3.9. Static dilution oven: laboratory oven capable of holding 60°C ± 10°C, with a mounted injection port. Flow-controlled helium supply to the injection port and a separate line for purging gas bulbs is included.

3.10. Thermal desorb unit: capable of desorbing tubes at 300–330°C. Must be capable of automated analysis.

3.11. Thermal desorber expendable supplies such as seals.

3.12. GCMS with computer hardware/software system capable of automated analysis and data reduction. GC must be capable of multiple ramp temperature programming and of cryogenic temperatures. Mass spectrometer must be able to generate classic electron impact spectra at 700 eV.

3.13. Sample tube conditioning oven: GC oven capable of maintaining 350°C, with a source of helium directed to a tube conditioning manifold. Manifold must be capable of holding 18 tubes.

4. Collection and Storage Requirements

4.1. Collection.

4.1.1. Collection procedures, including applicable quality control, are to be developed and implemented by the sampling personnel. Guidance is available from environmental chemistry personnel. Such procedures would include recordkeeping, sampling equipment calibration, flow verification, and measurement of field variables (such as temperature and pressure).

4.1.2. Sample tubes are directional. A flow-indicating arrow is painted onto each sample tube.

4.1.3. Samples should be taken in replicate, at different total volumes. See Source Material 12.2 for more information.

4.2. Storage.

4.2.1. Sample tubes are delivered in septa-sealed ampules. After sampling, replace tube in ampule. Place ampule in zipper-lock plastic bag. Place bags in paint cans containing activated charcoal.

4.2.2. Samples (after packaging as above) must be kept cold. At a minimum, place paint cans in ice-filled coolers in the field. Transfer to a freezer (-20°C) as soon as possible.

4.3. Holding time.

4.3.1. Hold time is 35 days after day of collection.

5. Reagents/Standards

5.1. Standards. Neat stocks of each compound are listed in Table I, found at the end of this procedure. They must be National Institute of Standards and Technology (NIST)-traceable. Compound group "A" must be purchased as a gaseous mixture in a cylinder.

6. Standards Preparation

6.1. Except for the group "A" compounds, static dilution gas-phase standards are to be used. These standards are prepared by injecting a known amount of liquid standard into a glass gas bulb. The gas bulbs are kept at an elevated temperature and contain glass beads for homogenizing the mixture. The liquid vaporizes, forming a gas-phase standard. Aliquots of this standard can then be injected onto the sample tubes.

6.2. Most of the group "A" compounds are in the vapor phase at room temperature and cannot be prepared in this manner. Purchase a commercial mix of these compounds in a gas cylinder.

6.3. Liquid intermediate standards.

6.3.1. Prepare liquid intermediate standards as follows. Using an analytical-grade syringe, measure an aliquot of each neat component and add to a septa-sealed vial. Keep the vial sealed and in an ice bath to avoid evaporation. Some components, namely trichlorotrifuoromethane and 1,1-dichloroethene, are measured cold, using a cold syringe, to avoid evaporation during sample transfer. Determine the amount (volume) of each component used by using the density of the compound, so that the resulting amount by weight is equal to 500 mg. The concentration of each component in the mix is 500 mg/final volume. Prepare these standards in "groups." The group, compound, density, and amount added (μL) are listed in Table II, found at the end of this procedure.

6.4. Static dilution standard preparation.

6.4.1. The volume of each gas bulb must be known. Heat the gas bulbs to 60°C, thoroughly purge with helium, and seal. Inject an aliquot of liquid standard into the bulb through the septa. Shake the gas bulb and allow it to equilibrate at 60°C for 30 min. Crack the seal on the bulb and quickly reseal to allow for pressure equilibration. The standard is now ready for use. The following table lists liquid standard final volumes and concentrations and the amount to add to a 2.0-L gas bulb to obtain the given gas-phase standard concentration:

	Group B	Group C	Group D	Group E	Group F
Final volume (μL)	9103	2482	7962	859	846
Liquid conc. (ng/μL)	54900	201000	62800	582000	591000
Amount to add to a 2-L gas bulb (μL)	91	25	80	9	8
Gas-phase conc. (ng/mL)	2500	2500	2500	2500	2500

7. Calibration

7.1. 4-Bromofluorobenzene (BFB) analysis. Before the analysis of any standards or samples, analyze 50 ng on column of BFB to check the performance of the mass analyzer. The mass spectra of BFB must meet the criteria listed below in Step 7.1.4 (from EPA SW846, method 8260).

7.1.1. From a 2500-ng/mL surrogate standard mix, spike 1.0 mL onto a clean tube. This results in 50 ng on column after the 1:50 split. The amount spiked depends on the concentration of the standard and the split ratio.

7.1.2. Analyze the surrogates using the same analyzer conditions that will be used for the standard and sample analyses.

7.1.3. Acquire a mass spectrum from the BFB peak. Acquire the mass spectrum using sound laboratory practices (see note in Step 7.1.4). Obtain a normalized tabulation of the masses of interest (a TUNER check report will suffice). If the spectrum fails criteria, take corrective action and reanalyze the surrogates.

7.1.4. The mass abundance ratios must meet the criteria listed below:

MASS	CRITERIA
50	15–40% of mass 95
75	30–60% of mass 95
95	Base peaks, 100% relative abundance
96	5–9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5–9% of mass 174
176	95–101% of mass 174
177	5–9% of mass 176

NOTE: Sound laboratory practices must be used when acquiring the BFB spectrum. The data cannot be manipulated for the sole purpose of obtaining a spectrum that passes criteria. For example, the spectrum at the chromatographic peak apex, the spectra on either side of the apex, or averaging around the apex may be used. These methods are valid because the apex spectrum may skew due to changes in concentration during acquisition. Subtraction of interfering background is also valid. However, practices such as subtracting a specific spectrum from another to change the response of a certain ion are not valid.

7.1.5. Standards and samples may not be analyzed until a valid BFB spectrum is obtained. All standard and sample analyses must be injected within 12 h of the injection time of the BFB analysis. This 12-h period is referred to as the "BFB clock."

7.2. Standards analysis.

7.2.1. Calibrate the system for the compounds of interest by analyzing standards with known concentrations of these compounds. Calibrate the instrument over the linear concentration range by analyzing standards at different concentration levels (initial calibration). After the initial calibration, check the instrument calibration by analyzing a single standard at a midrange concentration (continuing calibration). Samples may be analyzed after the initial and continuing calibrations meet the requirements listed below.

7.2.2. Initial calibration.

7.2.2.1. An initial calibration is needed if (1) the instrument is calibrated for the first time, (2) the continuing calibrations fail criteria (after taking other corrective actions), or (3) a major change has been made to the analytical system, such as cleaning the source or changing the column.

7.2.2.2. An initial calibration consists of analyzing standards at five levels, listed below. Spike five different tubes using the procedure in Sec. 8.2. Load the standards onto the thermal desorber. Use the same thermal desorber and GCMS conditions as are used for sample analysis.

Inject (mL)	Nanograms on tube
0.5	1,250
2.0	5,000
4.0	10,000
10.0	20,000
20.0	50,000

7.2.2.3. After the analysis of all standards is complete, quantitate each data file. Check each analysis for the following parameters:

- proper peak integration, especially the gases and freons,
- that all compounds were detected (the ID file must be edited if compounds are consistently missed), and
- run time and spectrum of each compound for proper identification, especially isomers or compounds that share common ions.

7.2.2.4. Load the quantitation data into a calibration file. Print out the data, showing response factors for each calibration point, the average response factor, average retention times, and percent relative standard deviation (%RSD) of the response factors.

7.2.2.5. The data must meet the following criteria before you proceed:

- %RSD for each compound must be less than 30%, <u>except for the following compounds for which 30% is considered a warning limit:</u>

  Dichlorodifluoromethane (a)
  Chloromethane (a)
  Vinyl chloride (a)
  Bromomethane (a)
  Trichlorofluoromethane (a)
  Bromoform (b)
  Methylene chloride (c)
  Carbon disulfide (c)

1,1,2,2-Tetrachloroethane (b)
Propylbenzene (d)
1,2,4-Trimethylbenzene (d)
1,3,5-Trimethylbenzene (d)
o,m, and p-Dichlorobenzene (d)
Acetone (e)
2-Butanone (e)
2-Hexanone (e)
4-Methyl-2-pentanone (e)

(a) Compounds may break through adsorbents or they may not desorb off the last phase.
(b) Sometimes exhibits low response factors.
(c) Common laboratory contaminants.
(d) Compounds may not thoroughly desorb off adsorbent materials.
(e) Compounds may exhibit erratic response factors because of poor desorption efficiency.

- Internal standards responses must be within 50–200% of the median internal standard response for the five-point initial calibration. Internal standard retention times (RTs) must not shift by more than ±0.5 min from the median RT.

- Injection time of all analyses must be within 12 h of the injection time of the BFB analysis. If time is left after the calibration is complete, blanks and samples may be analyzed after the standards, within the BFB clock. Samples are quantitated using the 5000-ng level.

7.2.3. Continuing calibration.

7.2.3.1. After initial calibration, analyze continuing calibrations on a daily basis (every 12 h) to confirm that calibration is still valid. Quantitate samples using the response factors of the continuing calibration. Analyze a continuing calibration after the BFB, and before the analysis of blanks and samples. Spike a clean tube using the procedure in Sec. 8.2 so that 5000 ng each of the target compound mix, internal standard, and surrogate mix is added to the tubes. Load the tube onto the thermal desorber. Use the same thermal desorber and GCMS conditions as are used for sample analysis.

7.2.3.2 After the analysis of the standard is complete, quantitate the data file. Check the analysis for the following:

- proper peak integration, especially the gases and freons,

- that all compounds were detected (the ID file must be edited if compounds are consistently missed), and
- run time and spectrum of each compound for proper identification, especially isomers or compounds that share common ions.

7.2.3.3. Load the quantitation data into a calibration file. Print out the data, showing response factors (RFs) for each compound, the average response factor from the initial calibration and percent difference (%D) of the continuing calibration RF from the average RF of the initial calibration curve.

7.2.3.4. The data must meet the following criteria before you proceed:

- %D for each compound must be less than 30%, <u>except for the following compounds for which 30% is considered a warning limit:</u>

  Dichlorodifluoromethane
  Chloromethane
  Vinyl chloride
  Bromomethane
  Trichlorofluoromethane
  Bromoform
  Methylene chloride
  Carbon disulfide
  1,1,2,2-Tetrachloroethane
  Propylbenzene
  1,2,4-Trimethylbenzene
  1,3,5-Trimethylbenzene
  o,m, and p-Dichlorobenzene
  Acetone
  2-Butanone
  2-Hexanone
  4-Methyl-2-pentanone

- Internal standard responses must be within 50–200% of the median internal standard response for the initial calibration or the previous day's continuing calibration. Internal standard retention time must not shift by more than ±0.5 min from the previous day's continuing calibration retention time.

8. Procedure

8.1. After the continuing calibration meets the requirements listed above, proceed with blank and sample analyses. The blank referred to is the system performance blank, a clean sample tube analyzed after standards are analyzed and before samples are analyzed to demonstrate system cleanliness. Analyze blanks in the same manner as samples.

8.2. Sample tube spiking.

8.2.1. Use the same method to spike standards onto tubes that is used for calibration and to spike surrogates and internal standards onto samples.

8.2.2. The injection port is mounted on the static dilution oven so that the effluent end is on the outside wall of the oven. This allows attachment of the tube to the injection port in a cold zone. Attach the tube to the injection port so that helium flow follows the flow-direction arrow painted on the tube. Tighten down the O-ring-sealed 0.25-in. fitting.

8.2.3. Remove the proper standard from the oven and shake to homogenize. Using a heated gas-tight syringe, remove an aliquot of standard. When coming to the syringe mark, hold for about 2 s to allow for pressure equilibration.

8.2.4. Remove the needle from the septa. Replace the gas bulb. Allow time for pressure equilibration. Inject the standard into the injection port by slowly pressing down on the syringe barrel. Allow about 2 min for the standard to purge onto the tube. Remove the tube and load it onto the instrument.

8.3. Spike internal standard/surrogate mix (IS/SU) so that 5000 ng is injected onto the tube (2.0 mL of 2500-ng/mL standard). Spike according to Sec. 8.2.

8.4. Load the sample tube(s) onto the thermal desorber following the manufacturer's directions.

8.5. Analyze using the proper thermal desorber and GCMS methods. Methods used for sample analysis must be the same used for standards analysis.

8.6. Samples and blanks must meet the following criteria for acceptance.

8.6.1. The blank must not have target compounds above the limit of quantitation. Do not proceed to sample analyses until a clean blank, meeting criteria in Steps 8.6.3 and 8.6.4, is analyzed.

8.6.2. All analysis injection times must be within the 12-h BFB clock.

8.6.3. Surrogate recoveries must be within 70–130%. If recoveries are moving out of this range during a quality control (QC) batch, stop analyses and correct the problem before proceeding.

8.6.4. Internal standard (IS) responses must be within 50–200% of the response of ISs in the daily standard analysis.

8.6.5. Target compounds must be within the linear calibration range.

8.7. Corrective actions.

8.7.1. Considering the nature of this analysis, reanalysis of a sample is not always possible. If samples were taken in replicate, reanalysis may be possible.

8.7.2. When replicates are taken at different total volumes, the higher volume sample may be analyzed first. If a compound concentration is above the linear range of the calibration curve, the lower volume sample must be analyzed.

8.7.3. If any of the above listed criteria were not met and a replicate is available, the replicate must be analyzed. If a replicate is not available, report the analysis. Document the out-of-criteria conditions in the case narrative.

9. Quality Control

9.1. Calibration.

9.1.1. 4-Bromofluorobenzene. A 50-ng on-column analysis of BFB is analyzed before analysis of any standards, blanks, or samples. Mass abundance criteria and proper spectrum acquisition techniques are listed in Sec. 7.1.4.

9.1.2. Calibration. An initial demonstration of instrument linearity must be performed before sample analysis. Check instrument calibration by analyzing continuing calibration standards on a daily basis. Sec. 7.2.2 gives the acceptance criteria and states when an initial calibration must be analyzed. Sec. 7.2.3 states the acceptance criteria for the continuing calibration.

9.2. Sample and blank criteria. Sec. 8.6 states the acceptance criteria for sample and blank analyses. Sec. 8.3 states the corrective actions taken when samples do not pass criteria.

9.3. Audit samples. A blind QC sample is provided by the Quality Assurance and Data Management (QADM) section. The QC sample is a liquid and QADM will

supply procedures for preparing a static dilution of the sample. Blind QC samples are analyzed at a frequency of 10%.

9.4. Documentation, data handling, and sample tracking.

9.4.1. The following logbooks and data handling procedures are used for pore gas analysis. The objective is to document all procedures done for this analysis, to document who does each task, and to meet Laboratory and Environmental Protection Agency (EPA) protocols.

9.4.2. All logbooks, including bound forms, must have a document number obtained from QADM. Besides the logs described below, other logbooks may be in use. All logbook entries must include the date, analyst signature, and a full description of the task being performed.

9.4.3. Instrument analysis log.

9.4.3.1. All analyses done on a given instrument are recorded in that instrument's logbook. Instrument logs are bound forms. Pages are consecutively numbered and are used consecutively. Unused lines of each page must be crossed out. The following information must be recorded:

- date,
- data system files (such as tune file and method file),
- standard codes for every standard used for the sample analyses (see Sec. 9.4.4),
- auto sampler (ATD) position,
- data file ID, sample ID, request number, matrix, sample volume, and analyst initial for each sample analysis. Standard analyses need data file ID, standard ID, and analyst initials,
- the injection time of the BFB check analysis used for the BFB clock and the injection time of the last analysis. If the last analysis is not within the 12-h clock, record the injection time of the last sample in the clock and mark the analyses outside the clock as unacceptable, and
- fill in the QC check section for each sample analysis. Indicate in each box if the criteria were met or not. Indicate if the analysis met all criteria. Circle the sample ID of the analyses that do not meet criteria.

9.4.4. Standards log.

9.4.4.1. The standard preparations log is a bound Laboratory notebook. All liquid static dilutions prepared daily are not logged. Standard preparations used for this analysis are recorded in this

logbook. Each page is used consecutively and unused sections of each page are crossed out. To facilitate identification of each standard preparation and to cross reference the standards to the analysis log, the following standard code ID used:

logbook document#:page:entry#:date

Example: R7061:173:1:121192 is a standard preparation entered in logbook R7061, page 173, the first entry on that page, and it was prepared on December 11, 1992.

9.4.4.2. Each standard preparation entry must have the following information:

- description of standard,
- date,
- analyst signature,
- components' description, manufacturer, lot # (or standard code of the component is a stock prepared in-house), and date opened. Diluent solvent is a component,
- amount of each component used, initial component concentration, final component concentration, and
- final volume.

9.4.4.3. Information such as manufacturer's stock standard labels may be permanently attached to the logbook. A form for the liquid stock standard preparation may be used and permanently attached to the logbook.

9.4.5. Instrument maintenance log.

An instrument maintenance logbook is provided for each analytical system. These logbooks are bound forms. All instrument maintenance, including routine maintenance, should be recorded in these logbooks. Major instrument maintenance, troubleshooting, and changes to analytical system configuration must be recorded. Include the date and analyst signature for all entries.

9.4.6. Refrigerator logs.

Temperatures of the standards and sample refrigerators must be recorded daily. A logbook is provided. This is a bound Laboratory notebook. Each entry must include the date, analyst initials, and the temperature in °C.

9.4.7. Data handling.

9.4.7.1. All data is organized and handled in the same manner so that each request may easily be worked on by different analysts at any point in the analysis/data reduction process.

9.4.7.2. Each request has a job folder, which is initiated when the initial service agreement is received. Each file includes

- analytical service agreement,
- analytical chemistry request,
- sample priority authorization form (if applicable), and
- radiochemistry screening results (if applicable).

9.4.7.3. These job folders are filed in a designated place at each analytical task area, in chronological order.

9.4.7.4. Each 12-h DFTPP clock is considered a QC batch. A folder is started for each batch. The folder includes

- DFTPP report,
- continuous calibration check or initial calibration check reports,
- sequence file report,
- medium QUANT reports for calibration analysis(es), and
- extended QUANT reports for sample data.

9.4.7.5. From each QC batch folder, a copy of the first four items above and the original sample data (including unreportable sample data) is filed in the appropriate job folder. Blank and QC analyses may need to be copied if this data pertains to more than one request. This data should be filed in the job folder and reduced on the same day as the initial data review. Data reporting should proceed as soon as possible.

9.4.7.6. Job folders and QC batch folders are stored in specific file cabinet spaces. Folders are organized chronologically. Job folders may be stored at the instrument bench while analyses are being performed. Access to these folders is limited.

9.4.8. Sample tracking.

9.4.8.1. Sample tracking is done on two levels: (1) all request numbers and total number of samples are tracked on the analyst task/request log and (2) samples per individual request are tracked in the job folder, on the sample extraction bench sheet.

9.4.8.2. The analyst task/request log is generated for each analyst who is assigned samples (all pore gas samples are assigned to the pore gas task leader). This log is generated from the LIMS data system and tracks samples by request number. It tracks samples per request, due dates, and hold times. As requests are analyzed, write status on the provided hard copy. When data is reported, the request number is taken off this list.

9.4.8.3. Each sample is also tracked on the service agreement. When samples are analyzed, check off that sample number. When a sample needs re-analysis, note on the service agreement.

9.4.8.4. When scheduling analyses, pay particular attention to hold times, data due dates, and request priority.

10. Data Interpretation

10.1. Qualitative analysis.

10.1.1. Compounds are qualitatively identified by mass spectrum and RT matching.

10.1.2. For a given target compound, a sample spectrum is matched to a spectrum acquired from the analysis of a standard. The mass spectrum must meet the requirements outlined in EPA method SW846. In particular, all masses present in the standard spectrum above 10% of the base mass peak must be present in the sample spectrum. Ratios between masses must not vary by more than 25%. However, if a sample spectrum does not meet these criteria, but the analyst feels the spectrum is a match, the compound may be reported. The analyst must note this on the data or in a case narrative.

10.1.3. RTs, relative to the internal standard used for quantitation, as well as mass spectra must also match. This is especially true with isomeric compounds, which have very similar mass spectra but can be distinguished from each other by RT.

10.2. Quantitative analysis.

10.2.1. Quantitation is done by the internal standard method using the average response factors from the continuing calibration analysis. Two internal standards are used. The internal standard closest in RT to a given compound is used to quantitate that compound using the equations listed below.

10.2.2. Calculations.

10.2.2.1. Response factor.

$$Rf = \frac{AREA_{Ci}}{AREA_{IS}} \times \frac{CONC_{IS}}{CONC_{Ci}} ,$$

where Rf = response factor,
$AREA_{Ci}$ = area of compound *i* (in standard),
$AREA_{IS}$ = area of internal standard,
$CONC_{IS}$ = total concentration of internal standard (ng), and
$CONC_{Ci}$ = total concentration of compound *i* in the standard (ng).

10.2.2.2. Amount on tube.

$$A = Rf \times \frac{AREA_{Ci}}{AREA_{IS}} \times CONC_{Ci} ,$$

where A = total concentration of analyte (ng),
Rf = response factor, and
$AREA_{Ci}$, $AREA_{IS}$, and $CONC_{Ci}$ are from the sample analysis.

10.2.2.3. Concentration.

$$C_i = A/SV ,$$

where C_i = concentration of compound *i* in the pore gas (μg/L),
A = total concentration of analyte (ng), and
SV = sample volume (mL).

11. Proper Waste Disposal Practices

11.1. This method generates very little hazardous waste when compared to solvent extraction methods. Most of the hazardous waste associated with this method is generated during the preparation of standards. The following procedures

must be followed when generating any amount of hazardous waste. The procedures below pertain to satellite storage areas.

11.2. General waste management.

11.2.1. Analysts within the Organic Analysis section must receive Waste Generator Training from Environmental Protection (ESH-8) within 90 days of their date of hire.

11.2.2. Wherever possible, minimize the generation of waste through reduction, reuse, or recycling. Wherever possible, segregate containers to reflect the nature of the hazardous waste and the eventual waste disposal methods. For example, chlorinated solvent wastes should be segregated from flammable, non-chlorinated solvents and >50-ppm contaminated waste. This is especially important in analysis areas where the waste generated is considered to be mixed waste.

11.2.3. Categorize the waste using an ESH-8 Waste Profile Form (WPF). ESH-8 must then approve the WPF and generate a WPF reference number. The WPF must be updated yearly.

11.2.4. At a satellite hazardous waste storage area, there is no time limit on waste storage; however, there is a volume limit of 55 gal. of total waste (solid and liquid). A Chemical Waste Disposal Request (CWDR) must be submitted to Waste Services (CST-17) for waste removal. A valid WPF must be submitted with the CWDR for each category of waste. It takes about 30 days from the time of submitting the CWDR to when the waste is picked up. Therefore, submit the CWDy
yyR before the 55-gal. volume limit is reached.

11.3. Solid waste.

11.3.1. Accumulate solid hazardous wastes (such as contaminated paper towels, pipettes, spent syringes, and glass vials) in a sealed metal or plastic container lined with a plastic bag. Label the container with a hazardous waste label that identifies the hazard, type of material being stored (such as pipettes or paper towels), and the laboratory of origin.

11.3.2. Open the waste container only for the amount of time necessary to add the waste.

11.4. Liquid waste.

11.4.1. Accumulate liquid wastes (such as spent solvents that are not reusable) in glass or steel containers appropriate for the type of sample being stored. For example, store caustic materials in glass containers and spent solvents that are not bound for recycling in metal containers.

11.4.2. Place all containers storing hazardous liquid materials within secondary containment. Label the container with a hazardous waste label which identifies the hazard, type of material being stored (such as nonchlorinated solvent waste), and the laboratory of origin.

11.4.3. Open the waste container only for the amount of time necessary to add the waste.

11.5. Unused samples.

11.5.1. Sample tubes can be conditioned for reuse. Sample tubes are not considered hazardous.

12. Source Materials

12.1. US Environmental Protection Agency, "Test Methods for Evaluating Solid Waste," *Physical/Chemical Methods*, 3rd ed., SW846 (1988).

12.2. "Compendium of Methods for the Determination of Toxic Organic Compounds in Air," US Environmental Protection Agency report EPA 600/4-84-041 (April 1984).

TABLE I. ANALYTES AND LIMITS OF QUANTITATION (LOQ)				
Group	Compound	CAS #	LOQ ($\mu g/L$)$_{(1)}$	LOQ (ng)$_{(2)}$
A	Trichlorofluoromethane	75694	1.0	500
A	Chloroethane	75003	1.0	500
A	Chloromethane	74873	2.0	500
A	Dichlorodifluoromethane	75718	2.0	500
A	Vinyl Chloride	75014	2.0	500
A	Bromomethane	74839	5.0	500
B	2,2-Dichloropropane	594207	1.0	500
B	Dibromomethane	74953	1.0	500
B	1,1,1-Trichloroethane	71556	1.0	500
B	1,2-Dichloroethane	107062	1.0	500
B	Chloroform	67663	1.0	500
B	c-1,2-Dichloroethene	156592	1.0	500
B	1,3-Dichloropropene (cis and trans)	10061015	1.0	500
B	1,2-Dichloropropane	78875	1.0	500
B	1,1-Dichloropropene	563586	1.0	500
B	Carbon Disulfide	75150	1.0	500
B	Tetrachloroethene	127184	1.0	500
B	Trichloroethene	79016	1.0	500
B	Trichlorotrifluoroethane	76131	1.0	500
B	1,3-Dichloropropane	142289	1.0	500
B	t-1,2-Dichloroethene	156605	1.0	500
B	1,1-Dichloroethane	75343	1.0	500
B	Bromochloromethane	74975	1.0	500
B	1,1-Dichloroethene	75354	1.0	500
B	1,1,2,2-Tetrachloroethane	79345	2.0	500
B	Carbon Tetrachloride	56235	1.0	500

TABLE I. ANALYTES AND LIMITS OF QUANTITATION (cont)				
Group	Compound	CAS #	LOQ (μg/L)$_{(1)}$	LOQ (ng) $_{(2)}$
B	1,1,2-Trichloroethane	79005	2.0	500
B	Methylene Chloride	75092	1.0	500
B	1,1,1,2-Tetrachloroethane	630206	1.0	500
B	Bromodichloromethane	75274	1.0	500
B	Chlorodibromomethane	124481	1.0	500
C	2-Hexanone	591786	1.0	500
C	Acetone	67641	1.0	500
C	2-Butanone	78933	1.0	500
C	4-Methyl-2-Pentanone	108101	1.0	500
D	Bromobenzene	108861	1.0	500
D	Bromoform	75252	1.0	500
D	Chlorobenzene	108907	1.0	500
D	Ethylbenzene	100414	1.0	500
D	1,3,5-Trimethylbenzene	108678	2.0	1000
D	Toluene	108883	1.0	500
D	m-Xylene	1330207	1.0	500
D	Benzene	71432	1.0	500
D	1,3-Dichlorobenzene (M)	541731	1.0	500
D	n-Propylbenzene	103651	1.0	500
D	o-Xylene	1330207	1.0	500
D	1,2,4-Trimethylbenzene	95636	2.0	1000
D	Styrene	100425	1.0	500
D	1,4-Dichlorobenzene (P)	106467	1.0	500
D	1,2-Dichlorobenzene (O)	95501	1.0	500
D	p-Xylene	1330207	1.0	500
E	Fluorobenzene (IS)	540363	N/A	N/A

TABLE I. ANALYTES AND LIMITS OF QUANTITATION (cont)				
Group	Compound	CAS #	LOQ (μg/L)$_{(1)}$	LOQ (ng)$_{(2)}$
E	Chlorobenzene-d5 (IS)	3114554	N/A	N/A
F	Toluene-d8 (SU)	2037265	N/A	N/A
F	4-Bromofluorobenzene (SU)	460004	N/A	N/A

GROUP: Used to sort compounds for convenience in standards preparation. Group "E" are internal standards and group "F" are surrogates.

Other compounds may be analyzed upon request.

(1) Limit of quantitation, assuming a 500-mL sample. Depends on sample volume.
(2) Limit of quantitation, total ng on tube. Accounts for sample split. Independent of sample volume.

TABLE II. COMPOUNDS, DENSITY, AND AMOUNT ADDED				
Group	Compound	CAS #	Density	Amount
B	2,2-Dichloropropane	594207	1.16	430
B	Dibromomethane	74953	2.50	200
B	1,1,1-Trichloroethane	71556	1.34	374
B	1,2-Dichloroethane	107062	1.26	398
B	Chloroform	67663	1.48	337
B	c-1,2-Dichloroethene	156592	1.44	346
B	1,3-Dichloropropene (c=71%, t=27%)	10061015	1.22	410
B	1,2-Dichloropropane	78875	1.16	431
B	1,1-Dichloropropene	563586	1.22	410
B	Carbon Disulfide	75150	1.26	396
B	Tetrachloroethene	127184	1.63	307
B	Trichloroethene	79016	1.46	341
B	Trichlorotrifluoroethane	76131	1.58	317
B	1,3-Dichloropropane	142289	1.16	431
B	t-1,2-Dichloroethene	156605	1.44	346
B	1,1-Dichloroethane	75343	1.17	428
B	Bromochloromethane	74975	1.99	251
B	1,1-Dichloroethene	75354	1.21	412
B	1,1,2,2-Tetrachloroethane	79345	1.59	315
B	Carbon Tetrachloride	56235	1.59	315
B	1,1,2-Trichloroethane	79005	1.44	347
B	Methylene Chloride	75092	1.33	377
B	1,1,1,2-Tetrachloroethane	630206	1.59	315
B	Bromodichloromethane	75274	1.98	253
B	Chlorodibromomethane	124481	2.45	204
B	t-1,3-Dichloropropene	10061026	1.22	410

TABLE II. COMPOUNDS, DENSITY, AND AMOUNT ADDED (cont)				
Group	Compound	CAS #	Density	Amount
C	2-Hexanone	591786	0.83	602
C	Acetone	67641	0.79	634
C	2-Butanone	78933	0.81	621
C	4-Methyl-2-Pentanone	108101	0.80	624
D	Bromobenzene	108861	1.50	334
D	Bromoform	75252	2.90	172
D	Chlorobenzene	108907	1.11	452
D	Ethylbenzene	100414	0.87	577
D	1,3,5-Trimethylbenzene	108678	0.86	579
D	Toluene	108883	0.87	577
D	m-Xylene	1330207	0.87	576
D	Benzene	71432	0.88	569
D	1,3-Dichlorobenzene (M)	541731	1.28	390
D	n-Propylbenzene	103651	0.86	580
D	o-Xylene	1330207	0.88	568
D	1,2,4-Trimethylbenzene	95636	0.88	570
D	Styrene	100425	0.91	551
D	1,4-Dichlorobenzene (P)	106467	Solid (mg)	500
D	1,2-Dichlorobenzene (O)	95501	1.30	384
D	p-Xylene	1330207	0.86	581
E	1,4-Difluorobenzene	540363	1.169	428
E	Chlorobenzene-d5	3114554	1.16	431
F	Toluene-d8	2037265	0.94	532
F	4-Bromofluorobenzene	460004	1.593	314

STRONTIUM-90 IN ENVIRONMENTAL MATRICES

Analyte: Strontium-90	**Method No.:** ER190
Matrix: Biologicals, soils, air filters, and waters	**Lower Limit of Detection:** 2.0 pCi/sample
Procedure: Beta counting of ^{90}Y	**Accuracy and Precision:** 99% ± 10%
Effective Date: 09/15/89	**Authors:** Bob B. Bates Richard J. Peters Daryl Knab

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.9 for proper waste disposal practices.

1. Principle of Method

1.1. Yttrium-90, the daughter product of ^{90}Sr decay, is removed from the sample by solvent extraction with bis(2-ethylhexyl) hydrogen phosphate (B_2EHHP).

1.2. After an ingrowth period, ^{90}Y is again extracted in B_2EHHP, back-extracted into an aqueous phase, precipitated as an oxalate, and beta-counted.

2. Sensitivity

2.1. Detection limits of 2.0 pCi/sample can be achieved. This translates into the following detection limits for our standard sample sizes:

1 pCi/g in soils (2.0-g aliquot),

0.2 pCi/g in biologicals (10-g vegetation ash or 10-g soft tissue aliquot), and

3.0 pCi/L in water (500-mL aliquot).

2.2 Lower limit of detection.

$$L_D = \frac{3 \times \sqrt{C_B}}{T_B \times 2.22 \times E \times Q \times R \times D \times G} ,$$

where L_D = "a priori" lower limit of detection,
C_B = counts for the blank sample,
T_b = time of the blank count,
2.22 = factor to convert dis/min to pCi,
E = counting efficiency,
Q = sample size (g or L),
R = fractional radiochemical yield for Y carrier,
D = correction for ^{90}Y decay before counting, and
G = correction for ^{90}Y growth after the first separation.

3. Accuracy and Precision

3.1. Water samples are spiked with known quantities of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4919-D ($^{90}Sr/^{90}Y$) and are periodically run through the entire chemical procedure.

3.2. There are no NIST SRMs for ^{90}Sr in water, biologicals, or air filters. NIST has several soil materials characterized for ^{90}Sr, but the concentrations are at fallout levels. The Environmental Protection Agency (EPA) circulates SRMs for ^{90}Sr in water, air filters, and foodstuffs as part of their radioactivity quality check program. The DOE Environmental Measurements Laboratory provides ^{90}Sr at elevated levels on all four matrices twice a year as part of their quality assurance program. Over a period of 2 years the determination of ^{90}Sr in these reference materials exhibited the following mean recoveries:

Matrix	Mean ± std dev	(n)
Biological	1.01 ± 0.23	33
Filters	1.02 ± 0.0	2
Soils	1.01 ± 0.18	18
Waters	0.93 ± 0.17	43

4. Interferences

4.1. Any beta-emitting nuclide is a potential interference.

5. Collection and Storage of Samples

5.1. No special precautions are required for soils, biologicals, and air filters. Filter and acidify water samples upon collection.

6. Apparatus

6.1. Separatory funnels: 250- or 125-mL, glass, with stopper.

6.2. Centrifuge.

6.3. Centrifuge tubes: 50-mL, glass.

6.4. Filter paper: Whatman No. 42 (7.0-cm) and No. 542 (2.4-cm).

6.5. Crucibles: Coors "0" size.

6.6. Millipore filtering apparatus: for 2.4-cm filters.

6.7. Nylon planchet: 1-in., with 6.8 Mylar covering to fit nylon planchet.

6.8. Tennelec low-beta counter: Model No. LB-4000.

6.9. Hot plate: with magnetic stirring capability, Corning Model No. PC-351.

6.10. Magnetic stirring bars.

6.11. Muffle furnace.

6.12. Platinum crucibles: 30-mL, with cover.

6.13. Analytical balance: with weights to 0.1 mg.

6.14. Drying oven.

6.15. Desiccator.

6.16. Beakers: 100-, 250-, 600-, and 1000-mL, Pyrex.

6.17. Beakers: 200-mL, Teflon.

6.18. Graduated cylinders: 10-, 100-, and 500-mL (use plastic when measuring HF).

6.19. Flasks: 500-mL, volumetric.

7. Reagents

7.1. B_2EHHP (20%). Dissolve 200 mL of bis(2-ethylhexyl) hydrogen phosphate in 800 mL of dodecane. Work in a fume hood. Store in glass.

7.2. B_2EHHP (5%). Dissolve 50 mL of bis(2-ethylhexyl) hydrogen phosphate in 950 mL of dodecane. Work in a fume hood. Store in glass.

7.3. Yttrium carrier (24 mg of Y_2O_3/mL). Dry Y_2O_3 at 100°C overnight. Cool and weigh 12.0 g into a 500-mL volumetric flask. Dissolve in approximately 26 mL of HCl. Dilute to 500 mL with distilled water and allow to stand overnight. Calibrate according to Step 8.3.

7.4. Hydrochloric acid (concentrated, reagent-grade).

7.5. Hydrochloric acid (2 M). Add 166 mL of concentrated HCl to 834 mL of distilled water.

7.6. Hydrochloric acid (0.08 M). Dilute 6.7 mL of concentrated HCl to 1 L with distilled water.

7.7. Ammonium hydroxide (concentrated, reagent-grade).

7.8. Ammonium hydroxide (6 M). Add 396 mL of concentrated NH_4OH to 604 mL of distilled water.

7.9. Nitric acid (concentrated, reagent-grade).

7.10. Nitric acid (3 M). Add 192 mL of concentrated HNO_3 to 808 mL of distilled water.

7.11. Ammonium oxalate solution (saturated). Add 50 g of ammonium oxalate to 1000 mL of distilled water.

7.12. Hydrogen peroxide (30%).

7.13. Hydrofluoric acid (concentrated, reagent-grade).

7.14. Boric acid, dry salt.

7.15. Boric acid solution (saturated).

7.16. Bromcresol green indicator solution.

7.17. Methyl orange indicator solution.

8. Calibration and Standards

8.1. A New England Nuclear Pa-234m standard, 0.0164 μCi, February 1972, has been used for a calibration check of the Tennelec LB-4000 low-beta counter. The standard is counted for 2 min each week whenever the counter is to be used.

8.2. Background counts of 200 min are taken every day the counter is in use.

8.3. Standardization of yttrium carrier.

8.3.1. Yttrium carrier should be calibrated monthly and/or at the time a new carrier solution is made.

8.3.2. Add 25 mL of 3 M HNO_3 and 1 mL of yttrium carrier to four 50-mL centrifuge tubes.

8.3.3. Add 10 mL of concentrated NH_4OH to precipitate the yttrium as a hydroxide.

8.3.4. Centrifuge for 5 min and discard the supernate.

8.3.5. Dissolve the precipitate in 5 mL of 2 M HCl. Allow time for complete dissolution.

8.3.6. Add 20 mL of distilled water and adjust the pH to between 1.4 and 1.7 (approximately 10 drops of concentrated NH_4OH).

8.3.7. Heat the samples in a hot water bath for at least 10 min. Add 2 mL of saturated ammonium oxalate. A precipitate should form.

8.3.8. Cool the samples and filter through tared 2.4-cm Whatman No. 542 filters. Using wash bottles, wash the sample with a minimum of distilled water and then alcohol.

8.3.9. Remove the samples from the filter tower, and place them in a preheated drying oven. Dry the samples at ~80°C for 30 min. Cool the samples for 20 min. Place the filters on an analytical balance and obtain the gross weight of the filter and precipitate. Record the weight.

8.3.10. Calculation. Calculate the average net weight ($\overline{X}$) of yttrium carrier using the table below.

Filter No.	Tare Wt.	Gross Wt.	Net Wt.	
1 _____	_____	_____	_____	
2 _____	_____	_____	_____	
3 _____	_____	_____	_____	
4 _____	_____	_____	_____	
		$\overline{X}$ =	_____	mg of yttrium carrier

9. Procedure

9.1. Begin using the ^{90}Sr data sheet (Fig. 1) as soon as sample analysis begins. Keep the data sheet up-to-date throughout the entire procedure; accurate times are necessary for the calculations.

9.2. Sample dissolution.

9.2.1. Soil dissolution.

9.2.1.1. Weigh a 2-g aliquot of a dry soil sample into a 200-mL Teflon beaker.

9.2.1.2. **CAUTIOUSLY** add approximately 100 mL of concentrated HNO_3. Carbonate soils can react vigorously. Add 100 mL of 48% HF.

CAUTION: HF is extremely hazardous. Refer to SOP-11, "Handling Hydrofluoric Acid," for the detailed safety policy. Wear rubber gloves, eye protection, and a lab coat. Completely clean up all spills and wash thoroughly after using HF. Make all HF transfers in an exhaust fume hood to avoid toxic fumes.

9.2.1.3. Boil the mixture to dryness.

9.2.1.4. Add 10 mL of concentrated HNO_3. **CAUTIOUSLY** add 30% H_2O_2 a few drops at a time from a squeeze bottle to oxidize any organic residues.

9.2.1.5. Evaporate the solution until the first salts appear. Repeat Step 9.2.1.4 until the solution is light yellow and clear.

9.2.1.6. Add 5 mL of HCl. Add 1 g of saturated H_3BO_3 if any HF was used.

9.2.1.7. Evaporate the solution until the first salts appear. Add 50 mL of HCl and 50 mL of H_2O. Transfer to 250-mL beaker.

9.2.1.8. Evaporate the solution until the first salts appear. Cover the beaker with plastic wrap until ready for solvent extraction.

9.2.2. Water samples.

9.2.2.1. Measure a 500-mL aliquot of the water sample into a 1-L Pyrex beaker.

9.2.2.2. Add 10 mL of concentrated HNO_3 and evaporate the solution to approximately 10 mL.

NOTE: A 1-L beaker on a Corning Model No. PC-351 hot plate set at "2" can be left unattended for 15 h (overnight).

9.2.2.3. Add 10 mL of concentrated HNO_3 and heat to boiling. When the sample begins steaming, **CAREFULLY** add 6 drops of 48% HF while swirling the sample. Evaporate until the first dry spots appear.

9.2.2.4. Carefully wash down the sides of the beaker with approximately 10 mL of concentrated HNO_3.

9.2.2.5. While heating the sample, add 30% H_2O_2 by drops to decompose any organic material. Repeated additions of concentrated HNO_3 and H_2O_2 may be required to completely ash some samples. The wet ashing is complete when the residue is white or very light yellow, and dry.

9.2.2.6. Perform Steps 9.2.1.5 through 9.2.1.8.

9.2.3. Vegetation dissolution.

9.2.3.1. Dry-ash the dried vegetation sample in a porcelain crucible at 300°C for 12 h in an ashing oven.

9.2.3.2. Raise the temperature to 500°C for 12 h or until the ash is white. Remove the sample from the oven and cool.

9.2.3.3. Weigh a 10-g sample of the ash into a 200-mL Teflon beaker. Perform Steps 9.2.1.2 through 9.2.1.8.

9.2.4. Tissue dissolution (including bone).

9.2.4.1. Weigh a 10-g aliquot of wet soft tissue or bone, excluding feathers or hide, into a 600-mL glass beaker.

9.2.4.2. Wet-ash with concentrated HNO_3 and 30% H_2O_2 until a clear or light yellow solution is obtained. Do not use HF.

9.2.4.3. Evaporate the solution until just dry.

9.2.4.4. Perform Steps 9.2.1.6 through 9.2.1.8.

9.2.5. Air particulate filter dissolution.

9.2.5.1. Place the air particulate filter in a 30-mL platinum crucible.

9.2.5.2. Record the crucible and sample number.

9.2.5.3. Place the crucible in a cold muffle furnace. Turn the furnace to 500°C and dry-ash for 4 h. Turn off the furnace. Remove the crucible and allow to cool for 30 min.

9.2.5.4. Add 5-10 mL of concentrated HF a few drops at a time to start. Cover with a platinum lid and let stand overnight.

NOTE: If glass fiber filters are used, ashing will not be complete.

9.2.5.5. Evaporate to dryness on medium heat.

9.2.5.6. Repeat the addition of HF followed by evaporation. Allow the sample to cool.

9.2.5.7. Carefully wash down the cover and sides of the crucible with approximately 5 mL of concentrated HNO_3.

9.2.5.8. **CAUTIOUSLY** add 1-2 drops of 30% H_2O_2 to the crucible. When the vigorous reaction subsides, repeat the addition of H_2O_2 until the solution is clear or straw-colored.

9.2.5.9. Evaporate the solution to approximately 1 mL.

9.2.5.10. Add 2 mL of saturated H_3BO_3 solution. Heat to dissolve the sample.

9.2.5.11. Transfer the solution to a 250-mL beaker with approximately 10 mL of concentrated HCl. Perform Steps 9.2.1.7 through 9.2.1.8.

9.3. First extraction procedure.

9.3.1. Add 25 mL of distilled water and let stand until dissolved.

9.3.2. Adjust the pH of the sample to approximately 1.4, determined by short-range pH paper, using 6 M NH_4OH or 2 M HCl. Transfer the sample to a separatory funnel. Filter through Whatman No. 42 paper if sample is not completely dissolved.

9.3.3. Add 25 mL of 20% B_2EHHP solution to the sample and shake for 2 min.

9.3.4. **Record the extraction time (T-1)** for later use in the calculations. Allow the phases to separate for at least 10 min.

9.3.5. For water samples, skip to Step 9.3.9.

9.3.6. Drain the aqueous (bottom) phase into the original beaker. Discard the organic (top) phase.

9.3.7. Add an additional 25 mL of 20% B_2EHHP to the sample. Pour the sample into the separatory funnel and shake for 2 min.

9.3.8. Allow the phases to separate for at least 10 min. Drain and discard the organic phase.

9.3.9. Drain the aqueous (bottom) phase into a clean 100-mL glass beaker. Adjust the pH to approximately 1.4 and add 1.0 mL of yttrium carrier.

9.3.10. Cover the beaker with plastic wrap and store the sample for at least 2 weeks to await ^{90}Y ingrowth.

9.4. Second extraction procedure.

9.4.1. If necessary, adjust the pH of the sample to approximately 1.4 using 6 M NH_4OH or 2 M HCl.

9.4.2. Add 25 mL of 5% B_2EHHP to the sample. Transfer to a separatory funnel and shake for 2 min.

9.4.3. Allow the phases to separate for at least 10 min. **Record the extraction time (T-2)** for later use in the calculations.

9.4.4. Drain the aqueous (bottom) phase into the original beaker and discard.

9.4.5. Add 25 mL of 0.08 M HCl to the organic phase in the separatory funnel. Shake for 1 min. Allow the phases to separate for at least 10 min. Drain the aqueous (bottom) phase and discard.

9.4.6. Add 25 mL of 3 M HNO_3 to the organic phase and shake for 2 min to extract the ^{90}Y. Allow the phases to separate for at least 10 min.

9.4.7. Drain the aqueous (bottom) phase into a 50-mL centrifuge tube. Add 10 mL of concentrated NH_4OH to precipitate the yttrium as a hydroxide.

9.4.8. Centrifuge the sample for 5 min and discard the supernate.

9.4.9. Dissolve the precipitate in 5 mL of 2 M HCl. Add 10 mL of distilled water, 1 drop bromcresol green, and 1 drop methyl orange.

9.4.10. Add concentrated NH_4OH until solution turns blue-green.

9.4.11. Add 2 M HCl until solution turns pink. Add 0.5 mL additional 2 M HCl.

9.4.12. Heat the sample in a hot water bath for 20 min. Add 2 mL of saturated ammonium oxalate to precipitate the yttrium as an oxalate.

9.4.13. Cool the sample and filter onto tared 2.4-cm Whatman No. 542 filters.

9.4.13.1. Wash the precipitate with a small amount of distilled water and follow with a small amount of alcohol.

9.4.13.2. While maintaining the vacuum, remove the chimney and air dry for 2 min to prevent curling of the filter paper.

9.4.14. Dry the samples in a drying oven for 20 min at approximately 80°C. Cool the samples for 20 min. Weigh the filter on an analytical balance to obtain the gross weight of the oxalate.

9.4.15. Mount the sample on a 1-in. nylon planchet with a Mylar covering.

9.4.16. Count the sample in a gas-flow proportional beta counter for 200 min (see Section 10).

9.4.17. **Record the midtime of counting (T-3)** for later use in the calculations.

9.4.18. Count the samples on the same day as they are precipitated for a minimum of ^{90}Y decay.

10. Counting Protocol for Strontium-90 Samples

10.1. Count samples within 24 h of the time they were precipitated to lessen the degree of ^{90}Y decay.

NOTE: Samples should not be counted within the first 7 h after the final extraction (T-2) to allow short-lived beta emitters to decay.

10.2. Load samples into the Tennelec LB-4000 four at a time and count for 200 min.

10.3. If sample activity is twice that of the background, recount the samples 12 - 72 h later for an additional 200 min. This checks for contamination in the sample.

10.4. Instrument quality control requirements.

10.4.1. Each week, run a 200-min background count.

10.4.2. Check instrument efficiency at the beginning of each workweek.

10.5. Verify the instrument settings for the Tennelec LB-4000.

- Timer: 200 min.
- HV switches: set at 1350 V. HV is software-controlled and should not be applied through the potentiometer on the front of the HV module.
- Power: ON.
- Flow rate of P-10 gas: set between 0.1 and 0.2.

Press the F1 key to start the counters.

10.6. Refer to the Tennelec LB-4000 manual and to Method No. CR230 for detailed counting instructions.

11. Calculations

The following calculations of radiometric counting data are performed for determinations made without a radiotracer. Most data values are assumed to have Poisson distributions, and all time-measurement errors are assumed to be insignificant.

11.1. Counting efficiency is a function of self-absorption of the beta particles in the precipitated sample. A series of 24 ^{90}Sr samples is prepared with varying amounts of yttrium carrier. The calculated efficiency of the mounted samples is plotted against the mass of the precipitate to construct an efficiency curve as a function of yttrium recovery. A least squares equation is calculated from the plotted data.

11.1.1. The counting efficiency of the counter for a single background and standard is given by

$$E = \frac{\left(\frac{C_s}{T_s} - B\right)}{A_s \times K} ,$$

where E = efficiency (counts per disintegration),
C_s = gross counts for the standards,
T_s = counting time for standard (min),
B = background count rate (counts/min),

A_s = activity of the standard (dis/min), and
K = the ^{90}Y growth factor times the ^{90}Y decay factor times the Y recovery.

11.1.2. Average efficiency.

$$\overline{E} = \frac{\sum_{i=1}^{n} E_i}{n} ,$$

where $\overline{E}$ = average efficiency,
E_i = individual efficiencies, and
n = number of E_i values.

11.1.3. The standard deviation of $\overline{E}$ is

$$SD(\overline{E}) = \sqrt{\frac{\sum_{i=1}^{n} (E_i - \overline{E})^2}{(n-1)n\overline{E}^2} + \frac{SD(A_S)^2}{(A_S)^2}} ,$$

where $SD(\overline{E})$ = standard deviation of $\overline{E}$ (counts per disintegration),
E_i = counting efficiency,
$\overline{E}$ = average efficiency,
n = number of values used for the efficiency calculation,
A_S = activity of the added standard, and
$SD(A_s)$ = standard deviation of the standard solution activity.

11.2. Background.

11.2.1. The background count rate is

$$B = \frac{C_b}{T_b} ,$$

where B = background count rate (counts/min),
C_b = gross counts for the background, and
T_b = counting time for the background (min).

11.2.2. The standard deviation for the background count rate is calculated by

$$SD(B) = \frac{\sqrt{C_b}}{C_b} ,$$

where SD(B) = standard deviation of the background and
C_b = individual background count.

11.3. Sample activity.

11.3.1. The activity of the samples is given by

$$A_x = \frac{\left(\frac{C_x}{T_x} - B\right)}{\bar{E}} ,$$

where A_x = sample activity (dis/min),
C_x = gross counts for the sample,
T_x = counting time for the sample (min),
B = background count rate (counts/min), and
$\bar{E}$ = average counting efficiency.

11.3.2. The standard deviation of the activity of the sample is given by

$$SD(A_x) = \frac{\sqrt{C_x}}{C_x} ,$$

where $SD(A_x)$ = standard deviation of sample activity (dis/min) and
C_x = gross counts for the sample.

11.3.3. The lower limit of detection of the activity for high-background instruments is determined to be three times the standard deviation of the background.

$$L_D = \frac{3 \times SD(B)}{K \times T_B} ,$$

where L_D = lower limit of detection,
SD(B) = standard deviation of the background count,
K = constant in sample units corrected for growth and decay, and
T_B = time of the background count.

11.4. Calculation to put the radiometric measurement into the required form for final reporting.

11.4.1. Reported activity.

$$ACT_x = \frac{A_x}{K \times Q \times Y \times D \times G} ,$$

where ACT_x = sample activity in correct units for reporting (usually pCi/L or pCi/g),
A_x = sample activity (dis/min),
K = conversion factor (2.22 pCi per dis/min),
Q = sample quantity analyzed (0.005 L),
Y = yttrium carrier recovery,
D = ^{90}Y decay, and
G = ^{90}Y ingrowth.

11.4.1.1. The ^{90}Y decay is given by

$$D = e^{-\ln 2 (T_3 - T_2) / T_{1/2}} ,$$

where T_3 = midpoint of count time in days,
T_2 = second separation time in days, and
$T_{1/2}$ = half-life of ^{90}Y (days).

11.4.1.2. The ^{90}Y ingrowth is given by

$$G = 1 - e^{-\ln 2 (T_2 - T_1) / T_{1/2}} ,$$

where T_2 = second separation time in days,
T_1 = first separation time in days, and
$T_{1/2}$ = half-life of ^{90}Y (days).

11.4.2. The propagated uncertainty of the reported activity is

$$U_x = |ACT_x| \times \sqrt{SD(A_x)^2 + SD(E)^2 + SD(Q)^2 + SD(R)^2 + SD(B)^2} ,$$

where U_x = propagated uncertainty of the reported activity,
ACT_x = reported activity,
$SD(A_x)$ = standard deviation of sample activity,
SD(E) = standard deviation of the efficiency,
SD(Q) = standard deviation of the sample quantity,
SD(R) = standard deviation of the yttrium carrier recovery, and
SD(B) = standard deviation of the background.

11.5. Computer listing. The actual data calculations are calculated by a FORTRAN program within the VAX computer.

12. Proper Waste Disposal Practices

12.1. Liquid waste.

12.1.1. Collect the dodecane-HDEHP solution from Steps 9.3.6 and 9.4.7 in a loosely sealed glass bottle, labeled as organic waste.

12.1.2. Discard the acid solution from Step 9.4.4 into the acid waste system.

12.1.3. Discard the supernate from Step 9.4.8 into the acid waste system.

12.1.4. Discard the filtrate from Step 9.4.13.2 into the acid waste system.

12.2. Discard the mounted ^{90}Y sample in the normal waste after two weeks.

12.3. Waste pickup.

12.3.1. Fill out the Waste Profile Form and send it to Waste Management (CST-7).

12.3.2. Give the approved Waste Profile Form and waste container to the Environmental Chemistry (CST-9) waste coordinator.

12.3.3. CST-7 picks up the waste for disposal in accordance with Laboratory policy in Administrative Requirement 10-3.

13. Source Materials

13.1. *EML Procedures Manual*, 26th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, US Department of Energy, New York, HASL-300, 1986).

13.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

13.3. "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," US Environmental Protection Agency, EPA 600-4-80-032, pp. 58-74 (August 1980).

13.4. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Waste Water*, 16th ed. (American Public Health Association, Washington, DC, 1985).

13.5. Branch Technical Position, Revision I, Regulatory Guide 4.8, Radiological Assessment Branch, Nuclear Regulatory Commission (November 1979).

13.6. "American National Standard for Performance Criteria for Radiobioassay," draft, American National Standards Institute, ANSI N13.30 (1989).

13.7. L. A. Currie, "Limits for Qualitative Detection and Quantitative Determination," *Anal. Chem.* 40, 586-593 (1968).

13.8. "Standard Methods for the Examination of Water and Waste Water," R. Popper, Ed. (American Public Health Association, 1976).

13.9. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked the entire section has been revised.

STRONTIUM-90 DATA SHEET

Request No._____ T-1_____(date/time) Y Carrier (mg)_____

Owner_____ T-2_____(date/time)

Matrix_____ Ingrowth Factor_____ Technician_____

Sample No.	Aliq. (g or l)	Eff	Y Carrier Rec		Filters (mg) Gross	Tare	Net	Sample Count	Sample cpm	Blank cpm	T-3 (date/time)	Decay Factor	Count Time(min)	Activity(pCi)
								First						
								Second						
								Third						
								First						
								Second						
								Third						
								First						
								Second						
								Third						
								First						
								Second						
								Third						

Data File _____

Control File _____

Storage Disk No. _____

Log Book Page No._____

A09643

Fig. 1. Strontium-90 data sheet

TRITIUM IN ENVIRONMENTAL MATRICES — DISTILLATION AND LS

Analyte: ^3H as tritiated water	**Method No.:** ER210
Matrix: Air, soil, biologicals, and water	**Minimum Detectable Activity:** 2.5 pCi total activity, or 500 pCi/L per 5-mL sample
Procedure: Distillation and liquid scintillation counting	**Accuracy and Precision:** 97% ± 14%
Effective Date: 04/15/84	**Author:** Richard J. Peters George H. Brooks

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.5 for proper waste disposal practices.

1. Principle of Method

1.1. Tritiated water is distilled from the sample and pipetted directly into a polyethylene liquid-scintillation vial to which a scintillation cocktail is added. Decay of ^3H is observed by liquid scintillation.

2. Sensitivity

2.1. Sensitivity is limited by count length and the detector background.

2.2. For routine measurements with a 60-min count length, the minimum detection limit (3 sigma above background) is 2.5 pCi of total activity. This equals 500 pCi/L for distilled 5-mL water samples. The minimum detectable level for air samples with a total air volume of 10.2 m^3 and a silica gel mass of 15 g equals 0.7 pCi/m^3.

3. Accuracy and Precision

3.1. There are no reference materials available from any agency for tritium in biological or silicate matrices.

3.2. There are no National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) for dilute tritium in water. Both Environmental Protection Agency (EPA) and Environmental Measurements Laboratory (EML) quality assurance programs circulate intercomparison samples of tritium in water. We also prepare quality control (QC) in-house materials for tritium in

water and soil. Over a period of six years the determination of tritium in these QC materials had a mean recovery of 97% ± 14% on 892 measurements.

4. Interferences

4.1. Low-energy activity from other isotopes in the sample may result in positive interference.

4.2. Light-absorbing or light-scattering materials may result in negative interference (quenching).

4.3. Interferences from Steps 4.1 and 4.2 are minimized as follows.

4.3.1. Distill samples that were previously analyzed without distillation.

4.3.2. Simple redistillation is probably not effective for samples that were previously distilled. Redistillation using an oxidizing agent such as potassium permanganate and refluxing may eliminate volatile organic codistillates.

4.4. Internal luminescence of the samples or cocktail may result in positive interference.

4.4.1. This interference is usually reduced by permitting samples to equilibrate in the chilled, dark counting chamber of the liquid scintillation counter for 2 h before actual counting.

4.4.2. Repetitive counting of samples to determine the half-life for "long-lived" luminescence and calculation of a correction factor is a second method for reducing this form of interference.

5. Collection and Storage of Samples

5.1. There are no special collection and storage requirements for water samples.

5.2. Water vapor from air samples is collected on silica gel and distilled from a closed system.

5.3. Freeze biologicals and soils at the time of collection and thaw just before distillation.

NOTE: These samples must **NOT** be air or oven dried.

6. Apparatus

6.1. Beakers: 50-, 600-, and 1000-mL, Pyrex.

6.2. Scintillation counting vials: 25-mL, polyethylene, with plastic caps.

6.3. Pipette: Oxford Macro, with 5-mL disposable tips.

6.4. Hot plates.

6.5. Watch glasses.

6.6. Filter apparatus with 0.45-μm membrane.

6.7. Centrifuge tubes: 50-mL, glass.

6.8. Liquid scintillation counter: Packard Model 2200CA or 2500TR.

6.9. Kimwipes.

6.10. Heating mantles.

6.11. Round-bottom flasks: 250-mL.

6.12. Distillation apparatus.

7. Reagents

7.1. Liquid scintillation cocktail: Ultima-Gold or other similar commercial product. Evaluate each new lot number to assure reproducibility of results.

7.2. Low-tritium-background water.

7.3. Methanol.

7.4. Potassium permanganate.

8. Calibration, Quality Assurance Materials, and Blanks

8.1. Calibration.

8.1.1. To provide accurate analysis for each type of matrix encountered, you must establish matrix-specific calibration curves.

8.1.1.1. Prepare a set of 10 samples within the matrix-specific liquid scintillation cocktail (10 mL for the bioassay program and 15 mL for the environmental program).

8.1.1.2. All samples will be overspiked with equal levels of ^{3}H standard (determine the amount that will provide adequate counting statistics within a reasonably short time).

8.1.1.3. Prepare a concentrated salt solution (5 g NaI + 40 mL deionized H_2O) as the quench agent.

8.1.1.4. Vary the amount of quench agent that is added to each of the 10 samples (usually ranging from 0 - 70 μL).

8.1.1.5. Count the samples in the liquid scintillation counting system. Use the appropriate counting protocol for the matrix of interest (i.e., bioassay or environmental program).

8.1.1.6. When initializing the liquid scintillation system, provide the appropriate input for the quench curve program. This will require the amount of standard added to the samples, the decay date of the standard, and any additional information that may be added to the comment field.

8.1.1.7. After the counting cycle is complete, the quench curve information will need to be copied to the counting protocols for the 2200CA counting system. The information is used automatically by the 2500TR counting system.

8.2. Quality assurance materials.

8.2.1. Open quality assurance materials.

8.2.1.1. Prepare a set of samples that match the matrix of interest in the sample-to-cocktail load.

8.2.1.2. Make several sets of various overspikes using a NIST ^3H standard, 4361B-57. Suitable activity ranges are 100 - 1000 pCi/L for the environmental program and 1000 - 10,000 pCi/L for the bioassay program.

8.2.1.3. Document the activity levels in the various QCs as a permanent marking upon the samples.

8.2.1.4. These samples can be run with any sample set. The information gathered from the analysis of these samples will provide the count room personnel with a high degree of confidence that the current set of samples that were analyzed were completed within acceptable analytical limits.

8.2.2. Blind quality assurance materials.

8.2.2.1. Blind QC samples are usually run with every set. These samples are prepared by the Quality Assurance section within the Environmental Chemistry group. The QCs are submitted

with the sample set; the specific samples are unknown to the analyst.

8.2.2.2. The samples are run with the routine samples. The exact nature of the samples are not known until final data reduction and report generation have taken place.

8.3. Blanks.

8.3.1. Matrix blanks should be run with every set.

8.3.1.1. Run three sample blanks prepared from deep-well water with each sample set.

8.3.1.2. Remake these samples every six months.

9. Procedure

9.1. Soil samples (see Fig. 1).

9.1.1. Fill a tared 600-mL beaker to approximately 2/3 capacity with soil from which water is to be distilled. Weigh the beaker and sample. Record the beaker weight and the sample weight.

9.1.2. Place a 50-mL beaker in the center of the soil so that about half the depth of the beaker is buried in the soil.

9.1.3. Place a clean watch glass on top of the 600-mL beaker and seal around the edge with plastic wrap.

9.1.4. Place ice in the watch glass and put the whole assembly on a hot plate. Set heat to maximum. Water will distill from the soil, condense on the underside of the watch glass, and drip into the 50-mL beaker.

9.1.4.1. Additional ice may be needed in the watch glass as the distillation proceeds.

9.1.4.2. If the soil is wet, use a lower heat setting on the hot plate to keep soil from spattering into the collected water.

9.1.5. Collect approximately 10 mL of water.

9.1.6. Pipet a 5-mL aliquot of the distillate into the counting vial.

9.1.7. Add 15 mL of scintillation cocktail to the vial and cap tightly. Shake the vial vigorously for a few seconds.

9.1.8. Label the cap of the scintillation vial with the sample number and submit to the counting facility for liquid scintillation counting.

9.2. Drinking water.

9.2.1. Filter the sample through a 0.45-μm membrane filter.

9.2.2. Pipette 5 mL of the filtrate into a 25-mL glass scintillation vial.

9.2.3. Perform Steps 9.1.7 through 9.1.8.

9.3. Sewage or turbid water.

9.3.1. If a gross alpha/beta determination has also been requested on these samples, measure 900 mL of the sample into a 1-L beaker. If only tritium is to be determined on these samples, use approximately 30 mL of sample in a 50-mL beaker.

9.3.2. Place the beaker on a hot plate.

NOTE: If several samples are treated at the same time, cover each beaker with plastic wrap to prevent cross contamination.

9.3.3. Place a large collection flask in a ring stand to one side of the hot plate turned so that the pouring spout of the collection flask is to the right of the beaker (Fig. 2). Cover the sample beaker and collection flask with plastic wrap except for a small section by the pouring spout.

9.3.4. Place a 50-mL beaker on a stand directly under the pouring spout of the collection flask to collect the water that will condense in the flask. Collect approximately 10 mL of water.

9.3.5. If the distillate is clear, perform Steps 9.1.6 through 9.1.8.

9.3.6. If the distillate is colored, redistill over potassium permanganate using reflux conditions. Note on the sample logsheet that this may be a problem sample requiring standard addition for quantitative analysis.

9.3.7. When the water collection is complete, rinse the collection flask with water and then with methanol. The collection flask must be completely dry before you use it for the next sample distillation.

9.3.8. If a gross alpha/beta determination has been requested, perform Step 9.4.1 of Method No. ER100.

9.4. Biological samples.

9.4.1. Analyze fresh or frozen samples that have NOT been air or oven dried. Fill a tared 600-mL beaker approximately 2/3 full with the biological sample from which water is to be distilled. Weigh the total sample.

9.4.2. Perform Steps 9.1.2 and 9.1.3.

9.4.3. Place ice in the watch glass and put the whole assembly on a hot plate (Fig. 1). Begin the distillation with a low heat setting (approximately 2) and increase the temperature slowly, being careful to minimize charring of the sample. The water will distill from the sample, condense on the under-side of the watch glass, and drip into the 50-mL beaker. Additional ice may be needed in the watch glass as the distillation proceeds.

9.4.4. Collect at least 6 mL of water. Achieving the preferred minimum of 10 mL may be very difficult for some types of biological samples.

9.4.5. If the sample is clear, perform Steps 9.1.6 through 9.1.8.

9.4.6. If the distillate is colored, redistill the sample over potassium permanganate using reflux conditions. Note on the sample logsheet that this may be a problem sample requiring standard addition for quantitative analysis. Perform Steps 9.1.6 through 9.1.8.

9.5. Silica gel cartridges.

9.5.1. Obtain the necessary number of centrifuge tubes. Mark the top of each tube with the sample number.

9.5.2. Weigh each centrifuge tube (with the cap on) to determine a tare weight of the tube. Use the styrofoam holders that the tubes come in as a stand to hold them on the balance.

9.5.3. Set up the distillation apparatus in the hood. This will require that the condenser be connected to the cold water supply. Raise the pressure of the water to provide an adequate flow through the condenser.

9.5.4. Carefully open the first silica gel cartridge. Empty the contents of the cartridge, through a funnel, into the round-bottom flask held in the heating mantle.

9.5.5. Replace the top of the condenser on the round-bottom flask. Place the other end of the condenser in the centrifuge tube. All the condensate will collect in this tube.

9.5.6. Turn on the rheostat then the switch.

NOTE: It is very important that the rheostat not be turned higher than 78% of the dial reading. The heating mantles are extremely susceptible to high voltages, which will cause the unit to fail prematurely.

9.5.7. It should take approximately 20-30 min for the mantle to reach the optimum temperature. You should notice a small amount of condensate within the condenser. If this is not seen, or the tube is cool to the touch, determine whether the unit is plugged in or the rheostat is working.

9.5.8. When the silica gel turns a deep blue (cobalt) in color, most (99%) of the moisture has been driven off and into the centrifuge tube. Turn off the rheostat and the switch.

9.5.9. Remove the condenser and pour the silica gel into a beaker. Let it cool before it is replaced in the cartridge.

9.5.10. Repeat Steps 9.5.4 through 9.5.9 for each successive sample.

9.5.11. Weigh each completed sample to determine the gross weight. Subtract the tare weight from the gross weight to determine the net weight of the sample. Record this weight; it will be required in the final report.

9.5.12. Perform Steps 9.1.6 through 9.1.8.

9.6. Moisture determination.

9.6.1. After extracting the tritium sample, place the samples in a drying oven overnight at a temperature suitable for the sample matrix.

9.6.2. Cool and weigh the samples. Return them to the oven for several hours. Cool and weigh the samples.

9.6.3. Repeat the drying until the weight loss is less than 1% of the sample weight. Record the final weight.

9.6.4. Some customers want the ash weight of the samples. For those samples, repeat Steps 9.6.1 through 9.6.3 at a temperature suitable for the sample matrix.

9.6.5. Use the dry or ashed sample for subsequent analyses.

10. Operation of Instrument

10.1. Loading the liquid scintillation counter.

10.1.1. Tighten the lid on the scintillation vial and shake vigorously to ensure complete mixing of the sample and cocktail.

10.1.2. Wipe the outside of the vial with a tissue and place the vial in the scintillation counter sample tray.

10.1.3. Write the sample number in the appropriate position on the tritium counting data sheet (Fig. 3).

10.1.4. Repeat the above procedure with the tray containing the standards and blanks. This tray should have the appropriate program indicator.

10.1.5. Place the samples within the sample tray in the following order: the three blanks, two samples, then the open QCs, then the remaining samples.

10.1.6. Place the samples within the liquid scintillation instrument and let them cool for approximately 30 min before beginning the count sequence. This will eliminate or at least minimize the effects of photoluminescent reactions.

10.2. To begin the counting sequence, depress the **F2** key on the 2200CA system or the **GREEN** button on the 2500 TR system. This will automatically load and count the samples, providing both a hard copy and a disk file for later transferral to the VAX system.

10.3. Simultaneously press the **ENABLE** and **FORWARD** keys on the counter to begin counting.

10.4. For further information concerning the operation of the instrument systems, refer to Method No. CR180.

11. Calculations

11.1. Calculations of radiometric counting data for determinations are made without a radiotracer. Most data values are assumed to have Poisson distributions and all time-measurement errors are assumed to be insignificant.

11.2. Counting efficiency.

11.2.1. The counting efficiency of the counter for a single standard run is calculated by the counter using an external standard and an established quench correction curve.

11.3. Background.

11.3.1. Background decompositions per minute are calculated by the counter. The calculation program averages three backgrounds to determine the mean background count.

11.3.2. The average background count rate is calculated by

$$\overline{B} = \frac{\Sigma_1^3 B}{3} ,$$

where $\overline{B}$ = average background count rate, and
B = background count rate.

11.3.3. The standard deviation for the average background count rate is calculated by

$$SD(B) = \sqrt{\frac{(B_i - \overline{B})^2}{n - 1}} ,$$

where $SD(B)$ = standard deviation of the average of the background,
B_i = individual background count rate,
$\overline{B}$ = average background from Step 11.3.2, and
n = number of values used.

11.4. Sample activity.

11.4.1. The activity in the samples is given by

$$A_x = (A - \overline{B}) ,$$

where A_x = net sample activity (dis/min per sample),
A = gross sample dis/min from the counter, and
$\overline{B}$ = average background count rate (counts/min).

11.4.2. The standard deviation of the activity in the sample is calculated by the scintillation counter using Packard proprietary equations.

11.4.3. The minimum detectable activity for high-background instruments is determined to be three times the standard deviation of the background:

$$MDA = \frac{3 \times SD(B)}{K} ,$$

where MDA = minimum detectable activity (dis/min),
SD(B) = standard deviation of the background count rate (counts/min), and
K = constant in sample units.

11.5. Calculation to put the radiometric measurement into the required form for final reporting.

11.5.1. Reported activity.

$$R_x = \frac{A_x}{K \times Q} ,$$

where R_x = sample activity in correct units for reporting (pCi/L),
A_x = sample activity (dis/min),
K = conversion factor (2.22 pCi per dis/min), and
Q = sample quantity analyzed (0.005 L).

11.5.2. The propagated uncertainty of the reported activity is

$$U_x = |R_x| \times \sqrt{\frac{SD(A_x)^2}{(A_x)^2} + \frac{SD(\overline{B})^2}{\overline{B}^2} + \frac{SD(Q)^2}{Q^2}} ,$$

where U_x = propagated uncertainty of the reported activity,
R_x = reported activity,
$SD(A_x)$ = standard deviation of sample activity,
$SD(\overline{B})$ = standard deviation of the average background,
SD(Q) = standard deviation of the sample quantity aliquoted,
Q = sample quantity aliquoted in reporting units,
A_x = sample activity (dis/min per sample), and
$\overline{B}$ = average background (counts/min).

11.6. Percent moisture content.

11.6.1. Percent moisture is calculated by

$$\% \ H_2O^- = \left(\frac{(W_W - W_T) - (W_D - W_T)}{(W_D - W_T)} \right) \times 100 \quad ,$$

where $\% \ H_2O^-$ = percent free water,
W_W = sample wet weight,
W_T = container tar weight,
W_D = sample dry weight, and
100 = conversion from weight fraction to percent.

11.6.2. Percent ash weight is calculated by

$$\% \ A = \left(\frac{W_A - W_T}{W_D - W_T} \right) \times 100 \quad ,$$

where $\% \ A$ = percent ash residue at a given temperature,
W_A = sample ash weight,
W_T = container tare weight,
W_D = sample dry weight, and
100 = conversion factor from weight fraction to percent.

12. Proper Waste Disposal Practices

12.1. Discard excess liquid samples into the acid waste drain system.

12.2. Save dried solid sample residues for subsequent analyses. If no additional analyses are requested, return the samples to the Sample Management section for disposal.

12.3. Dispose of the sample aliquot added to the liquid scintillation cocktail according to the Waste Management group procedure, "Scintillation Vial Disposal," and Administrative Requirement (AR) 10-3.

13. Source Materials

13.1. M. A. Tamers, "Liquid Scintillation Counting of Low Level Tritium," Packard Technical Bulletin No. 12 (June 1964).

13.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

13.3. "American National Standard for Performance Criteria for Radiobioassay," draft, American National Standards Institute, ANSI N13.30 (1989).

13.4 L. A. Currie, "Limits for Qualitative Detection and Quantitative Determination," *Anal. Chem.* 40, 586-593 (1968).

13.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

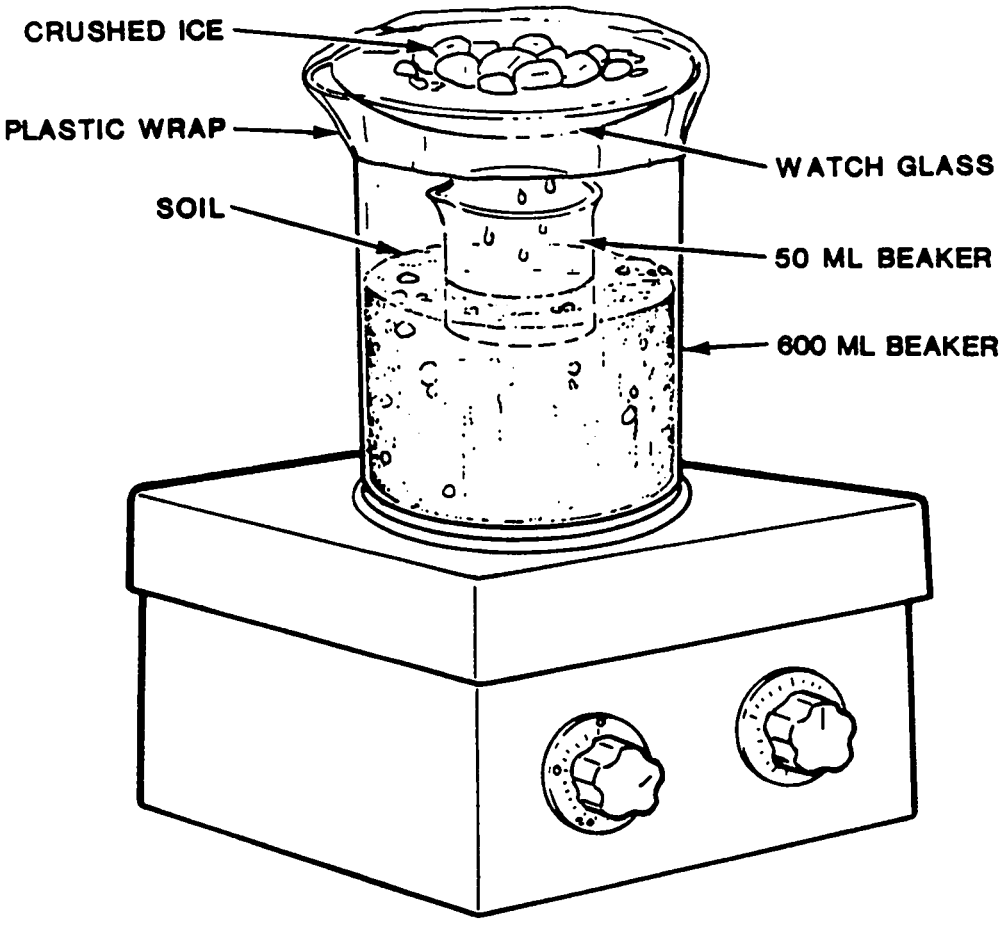

Fig. 1. Distillation apparatus for soil samples.

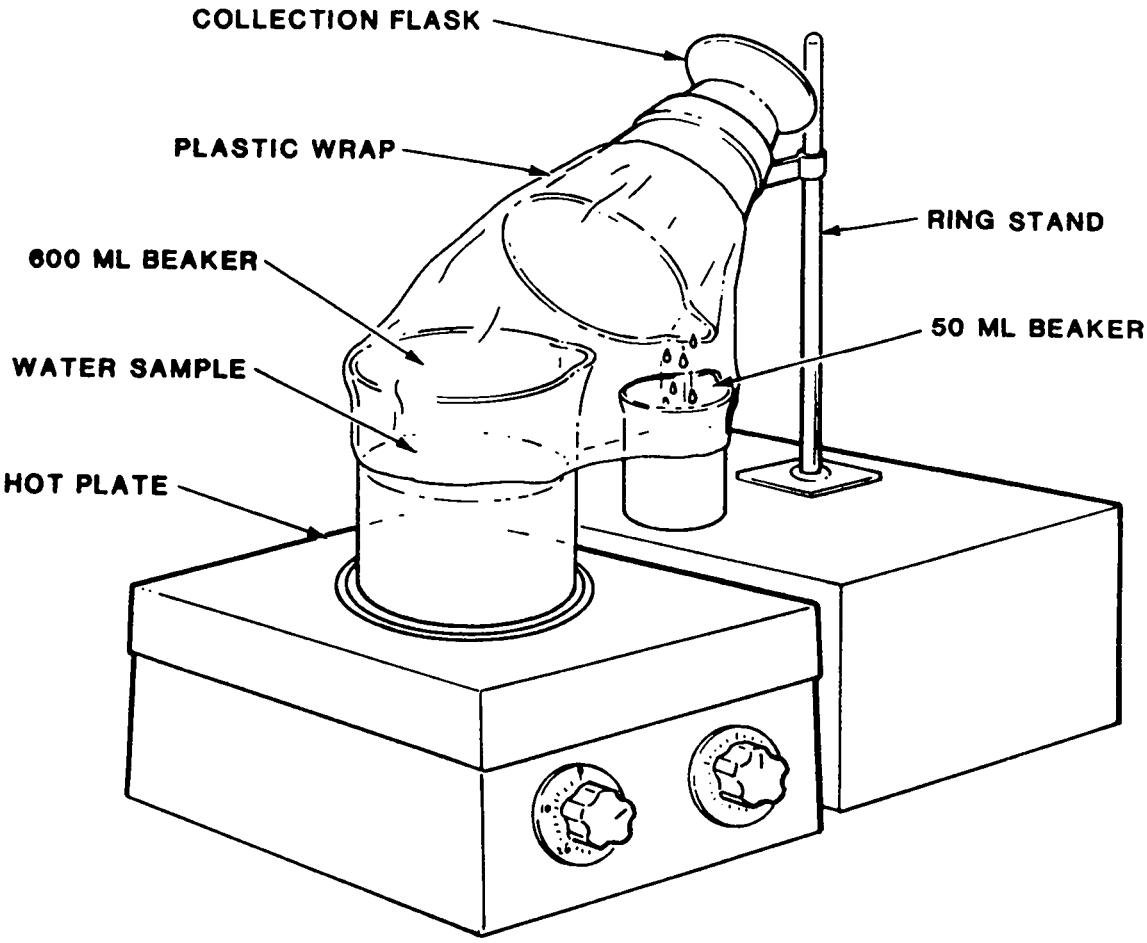

Fig. 2. Distillation apparatus for sewage or turbid water.

Program #= 5 01/05/90 13:21

REGION A: LL-UL= 0- 19 LCR= 0 BKG= .00 % 2 SIGMA= .0

REGION B: LL-UL= 2- 19 LCR= 0 BKG= .00 % 2 SIGMA= .0

REGION C: LL-UL= 0- 0 LCR= 0 BKG= .00 % 2 SIGMA= .0

TIME= 30.00 K= .033 QIP=SIE/AEC

P#	S#	Time	CPMA/K	%DEV	CPMB/K	%DEV	CPMC/K	%DEV	SIE	SIS	MIN
5	1	30.00	585.86	8.30	537.37	8.67	.00	.00	793.	26.121	32
5	2	30.00	585.86	8.30	549.49	8.57	.00	.00	789.	26.032	63
5	3	30.00	494.95	9.04	459.60	9.38	.00	.00	781.	27.242	94
5	4	30.00	429.29	9.70	416.16	9.85	.00	.00	557.	27.493	125
5	5	30.00	480.81	9.17	459.60	9.38	.00	.00	557.	27.316	157
5	6	30.00	469.70	9.27	445.45	9.52	.00	.00	558.	27.880	188
5	7	30.00	149783.	.52	137031.	.54	.00	.00	561.	13.092	219
5	8	30.00	1084.85	6.10	998.99	6.36	.00	.00	559.	20.483	250
5	9	30.00	1239.39	5.71	1149.50	5.93	.00	.00	558.	19.838	281
5	10	30.00	1144.44	5.94	1062.63	6.17	.00	.00	558.	20.602	312
5	11	30.00	487.88	9.10	463.64	9.34	.00	.00	575.	26.037	344
5	12	30.00	457.58	9.40	434.34	9.64	.00	.00	574.	26.943	375
5	13	30.00	443.43	9.55	415.15	9.87	.00	.00	576.	25.930	406
5	14	30.00	500.00	8.99	478.79	9.19	.00	.00	576.	26.611	437
5	15	30.00	454.55	9.43	428.28	9.71	.00	.00	572.	26.366	468
5	16	30.00	2546.46	3.98	2344.44	4.15	.00	.00	586.	16.822	500
5	17	30.00	458.59	9.39	439.39	9.59	.00	.00	574.	27.297	531
5	18	30.00	446.46	9.51	424.42	9.76	.00	.00	566.	27.158	562
5	19	30.00	505.05	8.94	486.87	9.11	.00	.00	573.	26.746	593
5	20	30.00	459.60	9.38	423.23	9.77	.00	.00	569.	26.180	624

Fig. 3. Tritium counting data sheet.

URANIUM IN ENVIRONMENTAL MATRICES—KPA

Analyte: Uranium	**Method No.:** ER320
Matrix: Soil, water, tissue, and vegetation	**Minimum Detectable Concentration:** Determined by sample
Procedure: Kinetic phosphorescence analysis (KPA)	**Accuracy and Precision:** 1-2% RSD
Effective Date:-03/01/93	**Authors:** Edward Gonzales Alice Slemmons

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 7. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.4 for proper waste disposal practices.

1. Principle of Method

1.1. The kinetic phosphorimetric analyzer (KPA) measures the sample's phosphorescence by logarithmically performing a least squares fit analysis of intensity or concentration versus decay lifetime (the time required for its phosphorescent intensity to decrease by the factor 1/e). This method provides a precise analysis for uranium concentration.

2. Sensitivity

2.1. Sensitivity is limited by the instrument response.

3. Accuracy and Precision

3.1. Precision of 1-2% relative standard deviation (RSD) is common. If, however, aliquots are measured gravimetrically rather than volumetrically, relative standard deviations on the order of 0.5% are possible at concentration levels over 1 μg/L and lifetimes longer than 200 μs.

4. Interferences

4.1. Colored agents absorb excitation or emission light.

4.2. Substances that cause short or zero lifetimes are quenching agents. Acidity may appear to quench because the enhancing complex may be dissociated.

4.3. Fluorescence from a contaminant may be strong enough to disrupt the normal decay curve of the analyte. This problem is indicated by curvature and a misplaced intercept.

4.4. Suspended particles interfere by strongly reflecting the laser beam. The reflected light will disrupt the normal decay curve of the analyte. This problem is indicated by curvature and a misplaced intercept. Eliminate the interference by centrifuging or filtering the sample through a 0.45-μm membrane filter before analysis.

4.5. Concentrated solutions of dissolved minerals, metals, or other substances may interfere by some of the above effects or by preventing complexation of the analyte with the enhancing reagent.

4.6. A chemical may interfere by complexing the analyte differently than the chosen reagent. The effect will be noted by a different lifetime.

4.7. A substance that holds the analyte out of the photoluminescence process causes static quenching and low results. An example is a complexant that maintains uranium as U^{+4}. Photoluminescent uranium is the UO_2^{++} ion.

4.8. A precipitate with either the analyte or enhancing reagent will interfere by loss and the particle effect.

4.9. Dirt or grease on the reference and sample cuvettes will cause interference. These cells must be scrupulously clean. Wash hands with soap and rinse well before handling. Only touch the top and bottom of the cell. For more on cuvette handling, see the KPA manual.

4.10. Chloride and reducing metals cause interference.

5. Collection and Storage of Samples

5.1. Water samples should be preserved at the time of collection by adding sufficient nitric acid to bring the sample pH to 2 or less.

5.2. Soil, biota, and air filters do not require preservation.

6. Apparatus

6.1. KPA-10 (kinetic phosphorescence analyzer): Chemcheck Instruments, Inc., or equivalent.

6.2. Muffle furnace.

6.3. Beakers: 30-mL, glass.

6.4. High temperature marker.

6.5. Balance.

6.6. Beakers: Teflon

6.7. Beaker covers: Teflon.

6.8. Stirring bars: Teflon-coated.

6.9. Hot plate-stirrer.

6.10. Pipettes: 1000-, 500-, and 100-μL, Eppendorf, removable tips or equivalent.

7. Reagents

7.1. Nitric acid (concentrated).

7.1.1. Nitric acid solution (5%). Dilute 50 mL concentrated HNO_3 to 1 L with deionized water.

7.1.2. Nitric acid solution (7.2 M). Dilute 458 mL of HNO_3 to 1000 mL with deionized water.

7.2. Hydrochloric acid (concentrated).

7.3. Hydrofluoric acid (48%).

7.4. Hydrogen peroxide solution (30%).

7.5. Metaphosphoric acid (2%).

7.6. Working standards. Standards should be brought up to volume using 5% nitric acid solution. They will be used for calibration, calibration checks, and standard additions. The concentrations of the standards should depend on the concentration range of the calibration and samples.

7.7. Deionized water.

8. Calibration and Standards

8.1. Calibration of the KPA.

8.1.1. Prepare the reference cell.

8.1.1.1. Fill the cell with a reference solution of 0.1-0.3 μg U in 2% metaphosphoric acid. Cap and mix. If degradation occurs, as

indicated by short lifetime or loss of linearity, the reference should be changed.

8.1.1.2. Place the reference cell in its holder next to the door hinge.

8.1.2. Measure the background.

8.1.2.1. Aliquot 1-2 mL, depending on sample and sensitivity requirements, of 5% nitric acid solution into the sample cell. Bring the volume to 3.0 mL with 2% metaphosphoric acid and mix. Place the cuvette in the cuvette holder. Close and latch the door.

8.1.2.2. Enter the CALIBRATION MENU. Hit **F1** to enter the calibration mode. Choose the high or low range and follow the computer instructions to start the measurement. When background has been measured, press **F1** to continue the calibration.

8.1.3. Identify the calibration standards.

8.1.3.1. Press **F2** to enter the standard concentrations and comments. If the units are different than the default units, press **F1** and enter the new units. The sample results will be in the units of the calibration.

8.1.4. Establish a calibration curve.

8.1.4.1. In the cell, aliquot the metaphosphoric acid and a standard solution in the same proportions as the blank. Follow the computer instructions to start the measurement. Choose another concentration and repeat. Do this until the calibration curve is complete. The calibration curve should have a minimum of three calibration points. Press **ESC** to get back to the MAIN MENU.

8.2. Standards should be prepared in a range of concentrations based on the range that will be used for establishing the calibration curve. They will be used for calibration and for standard addition measurements.

9. Procedure

9.1. Sample preparation.

9.1.1. Soil dissolution.

9.1.1.1. Weigh a 2-g aliquot of a dry soil sample into a 30-mL glass beaker. Label with a high-temperature marker.

9.1.1.2. Muffle for 2 h at 500°C.

9.1.1.3. Transfer the sample to a Teflon beaker. Add a Teflon-coated stirring bar.

9.1.1.4. **CAREFULLY** add approximately 40 mL of concentrated HNO_3. Carbonate soils can react vigorously. Add approximately 30 mL of 48% HF.

CAUTION: HF is extremely hazardous. Wear rubber gloves, eye protection, and a lab coat. Completely clean up all spills and wash thoroughly after using HF. Make all HF transfers in a exhaust fume hood to avoid toxic fumes. Refer to SOP-11, "Handling Hydrofluoric Acid."

9.1.1.5. Cover the beaker with Teflon beaker cover. Place on a magnetic-stirring hot plate and stir the sample overnight while heating.

9.1.1.6. A second leach with HF or $HF \bullet HNO_3$ may be needed if large quartz crystals are present. Finely suspended material will generally be dissolved in the subsequent boil down. Large amounts of certain mineral crystals, like magnetite or zircons, may require special treatment.

9.1.1.7. Evaporate the mixture to dryness.

9.1.1.8. **CAUTIOUSLY** add approximately 10 mL of concentrated HCl and approximately 5 mL of concentrated HNO_3. Boil down to remove the HF. Repeat until HF has been driven off.

9.1.1.9. Add 10 mL of concentrated HNO_3 and boil down to remove the HCl. Repeat.

9.1.1.10. Add 10 mL of concentrated HNO_3. **CAUTIOUSLY** add 30% H_2O_2 a few drops at a time to oxidize any organic residues. Continue adding HNO_3 and H_2O_2 until the solution is light yellow and clear.

9.1.1.11. Evaporate the solution.

9.1.1.12. Dissolve the residue in 7.2 M HNO_3.

9.1.2. Water.

9.1.2.1. If the water sample is clean, it can be analyzed directly.

9.1.2.2. If the sample is turbid or dirty, it will need to be wet-ashed.

9.1.2.2.1. Place 10 mL of sample into a clean glass beaker. Add 2-3 mL of concentrated HNO_3. While swirling, add 0.5 mL dropwise of 30% H_2O_2.

9.1.2.2.2. Set beaker on a hot plate at medium heat for several hours. Do not over dry the sample. Baking the sample will make it difficult to redissolve. Add 1 mL of HNO_3 and treat again with H_2O_2 until the sample is ashed pale yellow to white.

9.1.2.2.3. Dry the sample and dissolve in 10 mL of 5% HNO_3.

9.1.2.3. If this is not sufficient to clean up the sample, the water can be taken through a dissolution.

9.1.2.3.1. Measure a 25 mL aliquot of the water sample into a beaker. Add a few mL of concentrated HNO_3 and heat to boiling. **CAREFULLY** add 6 drops of 48% HF while swirling the sample. Evaporate to dryness.

CAUTION: HF is extremely hazardous. Wear rubber gloves, eye protection, and a lab coat. Completely clean up all spills and wash thoroughly after using HF. Make all HF transfers in an exhaust fume hood to avoid toxic fumes.

9.1.2.3.2. Wash down the sides of the beaker with approximately 5 mL of HNO_3. Add approximately 10 mL of concentrated HCl. Boil to drive off the HF. Repeat until the HF is gone. Add concentrated HNO_3 and boil to remove the HCl. Repeat.

9.1.2.3.3. Add 5 mL of concentrated HNO_3. While heating the sample, add 30% H_2O_2 dropwise to decompose any

organic material. Repeated additions of concentrated HNO_3 and H_2O_2 may be required to completely ash some samples. The wet ashing is complete when the residue is white or very light yellow, and dry.

9.1.2.3.4. Dissolve the residue in 5% HNO_3.

9.1.3. Vegetation.

9.1.3.1. Large samples are dried at 60°C in tared glass beakers (up to 4 L) until a constant weight is obtained on successive days.

9.1.3.2. Add 50 mL of distilled water to the beaker. Cover with perforated aluminum foil. Ash at 100-200°C for 8 h.

9.1.3.3. Ash at 300°C overnight.

9.1.3.4. Ash at 400°C for 8 h.

9.1.3.5. Ash at 500°C until the sample ash is completely white.

9.1.3.6. Cool and weigh the sample. Record the ash weight.

9.1.3.7. Repeat Steps 9.1.3.5 and 9.1.3.6 until a constant weight is achieved.

NOTE: The entire ash sample is frequently transferred to a 500-mL polyethylene bottle for gamma-emitting radionuclide analysis using Ge(Li) gamma-ray spectroscopy.

9.1.3.8. Dissolve the entire sample (up to 10 g) in approximately 200 mL of HNO_3. Add 1.00 mL of tracer(s) solution before continuing the dissolution.

9.1.3.9. Heat the sample on a hot plate and add 30% H_2O_2 in small amounts until the sample dries to a clear residue. The color may vary from pure white to deep lilac.

NOTE: Attention to the temperature is important because samples can bump violently if too hot.

9.1.3.10. Dissolve the residue in a mixture of 50 mL of concentrated HNO_3 and 25 mL of concentrated HCl. Boil to approximately 25 mL to remove the HCl.

9.1.3.11. Remove the sample from the hot plate and cool. Dilute to 100 mL with 7.2 N HNO_3. Let the sample stand overnight.

9.1.3.12. Filter the sample through a Whatman No. 42 filter paper. Rinse the beaker with 7.2 N HNO_3 to transfer all residue onto the filter paper. Save the filtrate for Step 9.1.3.17.

9.1.3.13. Return the filter paper and the residue to a 200-mL Teflon beaker. Add 100 mL of concentrated HF and 100 mL of concentrated HNO_3. Evaporate to dryness overnight on a hot plate set on low.

9.1.3.14. Dissolve the residue in 50 mL of concentrated HNO_3 and treat with 30% H_2O_2 as in Step 9.1.3.9.

9.1.3.15. Dissolve the residue in a mixture of 50 mL of concentrated HNO_3 and 25 mL of concentrated HCl. Boil to approximately 25 mL (all HCl is expelled). Add 5 g of H_3BO_3.

9.1.3.16. Cool the sample and dilute to 100 mL with 7.2 N HNO_3. Let the sample stand overnight.

9.1.3.17. Filter the sample through a Whatman GF/A glass-fiber filter into the beaker containing the filtrate from Step 9.1.3.12. Wash the filter to give a final volume (filtrate plus washings) of 300 mL.

9.1.3.18. Cover the beaker with plastic wrap until ready for ion-exchange separation.

9.1.4. Tissue dissolution (including bone).

9.1.4.1. Weigh a 10-g aliquot of wet soft tissue or bone, excluding feathers and hide, into a 600-mL glass beaker.

9.1.4.2. Add 1.00 mL of the appropriate tracer(s).

9.1.4.3. Wet-ash the sample with concentrated HNO_3 and 30% H_2O_2 until a clear or light yellow solution is obtained.

NOTE: Do not use HF because CaF_2 will precipitate.

9.1.4.4. Evaporate the solution until just dry.

9.1.4.5. Continue the procedure for water samples from Steps 9.1.2.7 through 9.1.2.10.

10. Operation of Equipment

10.1. Aliquot the sample into a cuvette. Add metaphosphoric acid and mix. The sample and metaphosphoric acid volumes should be in the same proportion as the calibration. If the sample size differs from the calibration size, include a dilution factor to correct the result back. Place the cell into the cuvette holder. Close and lock door.

10.2. To proceed from the MAIN MENU, press **F1**-Analyze. Type information into the fields and press ENTER. Following DESCRIPTION, a choice is available when both ranges are calibrated. Choose H or L for high or low. Enter dilution information under "Final Volume" and "Sample Aliquot Volume". Press **F1** to start the measurement.

10.3. Following the sample measurement, add 0.1-0.2 mL of a known concentration of uranium standard. The concentration should be approximately equal to the sample concentration. For standard addition calculations, see Steps 11.2.1 and 11.2.2.

10.4. An analytical report is obtained from each measurement. Sample ID, Date/Time, and Description are self-explanatory. Other information items are explained below.

10.4.1. Reference ratio. The value is the ratio of laser intensity during sample measurement divided by its intensity during calibration. This ratio is used to normalize fluctuations in laser power and temperature drift. The intensities are derived from reference data. The values should be between 0.8 and 1.2. If the value is below 0.8, prepare a new reference solution and remeasure the sample.

10.4.2. LASER pulses. The value is the number of laser pulses used in the measurement. See KPA manual to change selected value.

10.4.3. Lifetime. The value and uncertainty are in microseconds. Lifetime is reduced by increases in temperature and quenching agents, which may disrupt the analyte complex.

10.4.4. R^2. This is the correlation coefficient of linearity, which is close to 1.0 when data is near the theoretical straight line. When R^2 is less than expected, the decay plot should be inspected for an inaccurate result.

10.4.5. Cal. The calibration equation.

10.4.6. Intensity. Value displayed is intensity of first time gate used in the calculations. This provides a quick assessment of the measurement, particularly near the detection limit. The time delay of that gate is also shown.

10.4.7. Concentration. Result is given in units of calibration. The attached uncertainty is the standard deviation as calculated from the data and propagated with a fixed 1% in Low Range and 3% in High Range for pipetting error.

10.4.8. Dilution Factor. The calculated factor composed of the values input before the measurement. The analyst is responsible for entering consistent units and any conversion factors. The sample aliquot unit may be changed so that the analysis may be based on weight.

10.4.9. Integrated. This value is the integrated sum of all intensities within the analytical time window of time gates and is used in standard addition calculations.

10.4.10. Final Result. This is different from the concentration only when dilution factors have been input. It gives a result corrected for dilution or dissolution, in units of calibration (unless the volume unit was changed).

10.5. A standard addition measurement is usually necessary to correct for matrix effects in the sample. After the sample measurement, add 0.1-0.2 mL of a known quantity of standard to the cuvette and take another measurement. For calculations, refer to Section 11.2.

10.6. There are several special analysis modes which the analyst may want to use. For more information on the sample analysis program, refer to Section 10.8 of the KPA operation manual.

10.7. Also refer to the KPA manual for information on instrument setup and repair, trouble-shooting, and the KPA computer program.

11. Calculations

11.1. Instrument calculations.

11.1.1. All concentration calculations are performed by the data system. The computer calculates a least square regression to determine slope which, in this procedure, is the rate of sample decay versus the intensity intercept. The reference measurement adjusts all sample data to a fixed reference point, the reference mark. The first standard measurement in each range yields the reference mark, the intercept to which all other measurements are normalized. Refer to the KPA operations manual for a detailed description of the manipulation of this data. The acceptable minimum detectable amount (AMDA) for natural uranium with KPA methods is from 0.03-0.06 μg/L.

11.1.2. The calculation factor (K) may be calculated, as per ANSI N13.30, by using the following formula:

$$K = \frac{4.65 \times S_b}{MDA} ,$$

where s_b = standard error of the blank and
MDA = minimum detectable amount.

11.1.3. The relative bias for the text category (B_r) is calculated, as per ANSI N13.30, from each individual relative bias (B_{ri}) as follows:

$$B_{ri} = \frac{A_i - A_{ai}}{A_{ai}} ,$$

where A_i = the *i*th measurement in a category being tested and
A_{ai} = the actual quantity in the test sample.

$$B_r = \overline{B_{ri}} = \sum_{i=1}^{N} \frac{B_{ri}}{N} ,$$

where $\overline{B}_{ri}$ = the mean of B_{ri},
Σ = the summation of the B_{ri} values, and
N = the number of test samples in the category.

The relative bias for the test category (B_r) shall be within the -0.25 ± 0.50 range when A_{ai} is greater than or equal to 10 times the AMDA for any given radionuclide. Samples with quantities below 10 AMDA should be analyzed for periodic checking performance but should not be expected to meet performance criteria for B_r.

11.1.4. The relative precision (s_λ) for the sample analysis is calculated, as per ANSI N13.30, as follows:

$$S_\lambda = \left[\sum_{i=1}^{N} \frac{\left(\frac{A_i}{\overline{A}}\right)^2}{(N - 1)} \right]^{1/2} ,$$

where $\overline{A}$ = the mean of A,

A_i = relative dispersion of the values,
Σ = the summation of the A values, and
N = the number of test samples.

S_λ shall be in absolute values less than or equal to 0.4 when A_{ai} is 10 times the AMDA for any radionuclide. Test samples below 10 AMDA are not expected to meet the requirements for S_λ.

11.2. Other calculations.

11.2.1. Adjust the sample result to reflect the standard addition results as follows:

11.2.1.1. The addition of the known standard introduces a small dilution error into the measurement. Unless this is accounted for through the program, the analyst must correct for it before continuing.

11.2.1.2. To find the fraction of the standard addition recovered, subtract the sample measurement from the corrected standard addition measurement and divide this value by the known concentration added. The final sample result should be corrected by this recovery.

11.2.1.3. Example: measured sample value = 0.26 ng/mL. Known standard addition concentration = 0.25 ng/mL. Measured value of sample plus standard addition = 0.45 ng/mL.

$$\text{Recovery} = \frac{0.45 - 0.26}{0.25} = 0.76$$

$$\text{Value} = \frac{0.26\ \text{ng/mL}}{0.76} = 0.34\ \text{ng/mL}$$

11.2.2. Adjust for any dilutions that were not included in the sample analysis mode.

12. Proper Waste Disposal Practices

12.1. After counting the sample, discard metaphosphoric acid mixture into the acid waste system.

12.2. Return excess sample to the Sample Management section for disposal.

13. Source Materials

13.1. *Kinetic Phosphorescence Analyzer (KPA-10) Operation and Service Manual* (Chemcheck Instruments, Inc., Richland, Washington, 1990).

13.2. "Analysis of Total Uranium in Environmental Samples by Laser Kinetic Phosphorimetry," DN-R-003 (July 9, 1993).

13.3. R. Peters, D. Knab, and W. Eberhardt, "Plutonium in Environmental Matrices—Alpha Spectrometry," Method No. ER160, in *Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance*, Los Alamos National Laboratory manual LA-10300-M (most recent edition).

13.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

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Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance

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CHEMICAL OXYGEN DEMAND IN WATER AND WASTEWATER — AUTO ANALYZER OR MANUAL

Analyte: Chemical oxygen demand	**Method No.:** WI230
Matrix: Water and wastewater	**Range:** 10 - 500 mg/L
Procedure: Automated colorimetry	**Detection Limit:** 10 mg/L
	Accuracy and Precision: 97% ± 4% RSD
Effective Date: 04/29/86	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure and Source Material 11.5 for proper waste disposal practices.

1. Principle of Method

1.1. The sample is refluxed with hot sulfuric acid and a known excess of potassium dichromate to oxidize organic matter. The amount of Cr^{+3} formed is directly proportional to the concentration of organic matter originally present.

2. Accuracy and Precision

2.1. Auto analyzer procedure.

2.1.1. The determination of chemical oxygen demand (COD) in 15 Environmental Protection Agency (EPA) WP782/4 reference samples (232 ± 35 mg/L) over a period of 4 months gave a mean of 225 mg/L (97% recovery) and a relative standard deviation (RSD) of 4%.

2.1.2. Nine COD samples spiked at 40 mg/L over a period of 4 months gave an average recovery of 100% with an RSD of 11%. The recoveries ranged from 88% to 110%.

2.2. Manual procedure.

2.2.1. The determination of COD in 26 EPA WP782/4 reference samples (232 ± 35 mg/L) over a period of 8 months gave a mean of 220 mg/L (95% recovery) and an RSD of 14%.

2.2.2. Thirty-one COD samples spiked at 40 mg/L over a period of 4 months gave an average recovery of 96% with an RSD of 9.5%. The recoveries ranged from 78% to 120%.

3. Interferences

3.1. Traces of organic material from sampling bottles, glassware, the atmosphere, or reagents may cause gross positive error. Rinse all glassware with 20% H_2SO_4 to reduce contamination.

3.2. Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step. Minimize this loss by cooling the culture tube during addition of the sulfuric acid solution.

3.3. Chlorides are quantitatively oxidized by dichromate and represent a positive interference. The complexation of the chlorides by the addition of mercuric sulfate eliminates this interference.

3.4. Nitrite exerts a COD of 1.1 mg oxygen per mg nitrite. This interference is usually insignificant because of low nitrite levels.

3.5. Reduced inorganic species, such as iron and sulfide, are oxidized quantitatively under test conditions.

3.6. Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent.

4. Collection and Storage of Samples

4.1. Collect samples in glass bottles and immediately acidify to pH <2 with concentrated H_2SO_4. Store at 4°C.

4.2. Analyze biologically active samples as soon as possible.

4.3. Mix well those samples containing visible particulates to permit removal of representative aliquots.

5. Apparatus

5.1. Sampler IV: equipped with a 40-slot sample carousel and a 40/h, 3:1 sampling cam. Technicon, Tarrytown, New York.

5.2. Proportioning pump: Technicon, Tarrytown, New York.

5.3. COD manifold: equipped with pump tubes, mixing coils, and double delay coil. Technicon, Tarrytown, New York.

5.4. Colorimeter: equipped with 600-nm filter and 50- by 1.5-mm flow cell. Technicon, Tarrytown, New York.

5.5. Dual-pen strip-chart recorder: Technicon, Tarrytown, New York.

5.6. Spectrophotometer: Spectronic 88, Bausch and Lomb, Rochester, New York, or equivalent.

5.7. Pipettes: class A, volumetric, various sizes.

5.8. Pipettes: 2500-μL, Rainin electronic digital or equivalent.

5.9. Flasks: class A, volumetric, various sizes.

5.10. Culture tubes: Kimble glass disposable, 16- by 100-mm, with Teflon-lined caps. VWR Scientific, Los Alamos, New Mexico, or equivalent.

5.11. Oven: capable of maintaining constant heat of 150°C.

5.12. Hach COD reactor: catalog no. 45600-00, Hach Co., Loveland, Colorado (alternate).

5.13. Hach COD digestion reagent vials: low range, Hach Co., Loveland, Colorado (alternate).

6. Reagents

6.1. Sulfuric acid (concentrated, reagent-grade).

6.2. Silver sulfate (reagent-grade, crystal or powder).

6.3. Mercuric sulfate (reagent-grade, powder).

6.4. American Society for Testing and Materials (ASTM) Type I water.

6.5. Digestion solution. Dissolve 10.216 g of potassium dichromate ($K_2Cr_2O_7$) in 500 mL of ASTM Type I water in a 1-L volumetric flask. **Cautiously** add 167 mL of concentrated H_2SO_4 and 33.3 g of $HgSO_4$. Bring volume to about 900 mL and heat and stir on magnetic stirrer to dissolve. Cool and dilute to volume with ASTM Type I water.

6.6. Catalyst solution. Dissolve 22 g of Ag_2SO_4 in a 9-lb bottle of concentrated sulfuric acid (2200 mL). Stir for several hours on magnetic stirrer until dissolved.

6.7. Wash solution (50% H_2SO_4). Cautiously add 500 mL of concentrated H_2SO_4 to about 400 mL of ASTM Type I water in a 1-L volumetric flask. Set in an ice water bath. Mix, cool, and dilute to volume with ASTM Type I water.

6.8. Glassware wash (20% H_2SO_4). Cautiously add 200 mL of concentrated H_2SO_4 to about 700 mL of ASTM Type I water. Cool and dilute to volume with ASTM Type I water.

6.9. Diluent (0.2% H_2SO_4). Add 2.0 mL of concentrated H_2SO_4 to about 900 mL of ASTM Type I water. Dilute to 1 L.

6.10. Brij-35 (30% solution). Technicon, Tarrytown, New York.

6.11. Reagent water. Add 1.0 mL of Brij to 500 mL of ASTM Type I water.

7. Calibration and Standards

7.1. COD stock standard A (20 g/L). Dissolve 17.00 g of National Institute of Standards and Technology (NIST) standard potassium acid phthalate (previously dried for 2 h at 105°C and stored in a desiccator jar) in approximately 500 mL of ASTM Type I water. Dilute to 1 L and refrigerate. This standard is stable for 6 months.

7.2. COD stock standard B (2000 mg/L). Dilute 10 mL of stock standard A to 100 mL with diluent (0.2% H_2SO_4).

7.3. Working standards. Dilute the following volumes of stock standard B to 100 mL with diluent (0.2% H_2SO_4).

Stock Standard B (mL)	COD (mg/L)
1.25	25
2.5	50
5.0	100
7.0	140
10.0	200
15.0	300
20.0	400
25.0	500

7.4. Auto analyzer procedure.

7.4.1. Set the base line to zero using the base-line control knob on the colorimeter while pumping 50% H_2SO_4 instead of sample and with all pump tubes in their respective reagents. Set the highest-concentration standard to 100 on the chart paper using the **std. cal.** knob. Lower-concentration standards should read at 80, 60, 40, and 20 respectively. Record chart reading of standards in a Laboratory notebook.

7.5. Manual procedure.

7.5.1. Set the wavelength to 600 nm and adjust the blank reading to zero on the spectrophotometer. Read absorbence of standards and record in a Laboratory notebook or appropriate bench sheets.

8. Procedure

8.1. Digestion procedure.

8.1.1. To culture tubes (that have been rinsed with 20% H_2SO_4, ASTM Type I water, and air dried), add 2.5 mL of ASTM Type I water blank, standard, or sample with a Rainin 2500-μL electronic pipette. Reset the pipette to 1500 μL and add 1.5 mL of digestion solution to each tube. **Carefully** add 3.5 mL of catalyst solution down the side of the tube so that the acid forms a layer on the bottom of the tube. To prevent loss of volatile components, do not allow the layer to mix before capping the tube. Cap the tube tightly and let cool 5-10 min. Mix on a vortex mixer to mix the layers. Sample load must include at least 10% spikes, 10% duplicates, and 10% quality control samples. To spike a sample, add 1 mL of stock standard B to 50 mL of sample. The concentration of the spike is 40 mg/L.

8.1.2. Place all tubes, samples, blanks, and standards in an oven at 150°C. Heat for 2 h. Remove from oven and let cool to room temperature.

8.1.3. Alternate using Hach COD reagent vials (0 - 150 mg/L range). To each COD reagent vial, add one of the following: 2000 μL ASTM Type I water, standard, or sample. Cap tightly. Mix with vortex mixer. Place up to 25 vials in COD reactor set for 150°C for 2 h. Include a blank, four standards, and a laboratory control standard with each batch of 25 vials. Remove vials, invert, and let cool to room temperature.

8.2. Auto analyzer procedure.

8.2.1. Turn on the colorimeter, heating bath, and recorder and allow to warm up for 30 min. Use 50% H_2SO_4 in the wash receptacle.

8.2.2. Attach the COD manifold in line between the pump and colorimeter. Attach air lines to the segmenter tubes on the pump. Stretch the pump tubes across the brackets. Snap the platen into place. The pump will turn on automatically. Place reagent lines in the glassware wash solution and allow the system to wash for 20 min.

8.2.3. Place lines into the proper reagents and allow the pump to run until a steady base line is achieved. Set the base line to zero. Check the system for uniform bubble pattern, leaks, and adequate reagent supply.

8.2.4. Rinse all glassware and sample cups used in preparation of reagents, standards, and sample dilutions with glassware wash solution before use.

8.2.5. Run samples undiluted. Dilution adjustment may be necessary as evident on strip-chart output. Samples reading <10 on the chart should be rerun at higher concentrations if possible.

8.2.6. Load the carousel. Place duplicate sample aliquots next with a QC and blank every 10 samples. The last two positions should be a QC sample and blank. Insert a pin at the last position to automatically stop the carousel. If a second carousel is required, place midrange standards in positions 1 and 2 to check reproducibility of the calibration curve. If this standard does not agree to within ± 2 chart divisions with the previous run, the complete set of standards must be rerun.

8.2.7. When determinations are completed, place the reagent tubes in distilled water and rinse the system for a minimum of 10 min. Shut off power to the colorimeter and recorder. After rinsing, remove the reagent and wash tubes from the water and pump air until all visible liquid is

removed from the system. Shut down the pump by removing the platen. Release the pump tubes from the brackets.

8.2.8. Record chart readings in a Laboratory notebook. The average of the duplicate readings is reported. A very high sample, however, may bias the first peak of a low sample that follows. In this case, both values are recorded and the sample should be reanalyzed.

8.3. Manual procedure.

8.3.1. Set the wavelength control to 600 nm and zero the instrument on a blank. Read the absorbence of standards and samples and record in a Laboratory notebook.

9. Calculations

9.1 Auto analyzer procedure.

9.1.1. The factor to convert from auto analyzer chart reading to concentration can be calculated as follows:

$$F = \frac{Sc \times D}{100} \quad ,$$

where F = factor,
Sc = concentration of highest standard (mg/L), and
D = dilution.

$$C = F \times R \quad ,$$

where C = concentration of sample (mg/L),
F = factor, and
R = chart reading.

9.2 Manual procedure.

9.2.1. Calculate the linear least squares calibration line using the absorbences of the standards. The sample concentration is then calculated by substituting the absorbence as follows:

$$\text{CONC.} = \text{SLOPE} \times \text{ABSORBENCE} + \text{INTERCEPT} \quad .$$

9.3. COD spike recovery should be 40 mg/L ± 8.0 (allowable) or ± 4.0 (desirable).

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.4. Percent recovery should be between 80% and 120%.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where $\%R$ = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. Liquid waste.

10.1.1. Empty contents of reaction vials into a plastic-coated glass bottle that is kept in a secondary containment tray segregated from liquid waste containing cyanide or NH_3-N waste.

10.1.2. Label the bottle with a hazardous waste label indicating Ag, Cr, and Hg in contents.

10.2. Waste pickup.

10.2.1. When the bottle is full, request pickup by Waste Management (CST-7) by using the current Chemical Waste Disposal Request (CWDR). The current Waste Profile Form describing the waste is referenced on the CWDR.

10.2.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

11. Source Materials

11.1. Technicon Industrial Method No. 452-76W (Tarrytown, New York, 1977).

11.2. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 508C (American Public Health Association, Washington, DC, 1985).

11.3. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 410.4 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

11.4. A. M. Jirka and M. J. Carter, *Anal. Chem.* **47**, 1397 (1975).

11.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

SILICA IN WATER AND WASTEWATER — FLOW INJECTION

Analyte: Silica	**Method No.:** WI340
Matrix: Water and wastewater	**Range:** 1.0–100 mg/L
Procedure: Flow injection colorimetry using Lachat Quik Chem AE	**Detection Limit:** 1.0 mg/L
	Accuracy and Precision: 117% ± 6% RSD
Effective Date: 02/27/92	**Author:** Kathleen Straw

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. Soluble silica species react with molybdate under acidic conditions to form a yellow silicomolybdate complex.

1.2. This complex is reduced with 1-amino-2-naphthol-4-sulfonic acid (ANSA) and bisulfite to form a heteropoly blue complex that absorbs monochromatic light at 650 nm and 820 nm.

2. Accuracy and Precision

2.1. The determination of SiO_2 in 18 in-house quality control (QC) samples (40.0 ± 4.0 mg/L) over a period of 6 months had a mean of 47 mg/L and a relative standard deviation (RSD) of 6%.

2.2. Eleven samples spiked with 20–40 mg/L of SiO_2 over a period of 6 months had an average recovery of 96% with an RSD of 4%. The recoveries ranged from 90% to 102%.

3. Interferences

3.1. The interference from phosphates is eliminated by the addition of oxalic acid.

3.2. Tannin and large amounts of iron or sulfides interfere. Remove sulfides by boiling an acidified sample. Add ethylenediaminetetraacetic acid, disodium salt (Na_2EDTA) to eliminate the interference from iron.

3.3. Silica contamination may be avoided by storing samples, standards, and reagents in plastic and using American Society for Testing and Materials (ASTM) Type I water.

3.4. High fluoride concentrations can complex silica.

3.5. Oxidizing agents may interfere with color development.

3.6. High silica concentrations may precipitate.

4. Collection and Storage of Samples

4.1. Store samples in plastic bottles at 4°C.

4.2. Analyses must be completed within 28 days.

4.3. Filter all samples except drinking water.

5. Apparatus

5.1. Lachat QuikChem AE Flow Injection Analyzer System (Lachat Instruments, Milwaukee, WI 53218-1239).

5.1.1. Random Access Sampler (A11120).

5.1.2. Proportioning pump (A22100).

5.1.3. Sample-processing module (A24000).

5.1.4. Reaction module for QuikChem method #10-114-27-1-A.

5.1.5. Valve module (33900).

5.1.6. Master computer, IBM 386 SX, 25 MHZ, with color monitor and printer.

5.2. Pipettes: class A, volumetric, various sizes.

5.3. 1000-µL Eppendorf, disposable tips.

5.4. Plastic bottles: various sizes.

5.5. Flasks: various sizes, volumetric, Nalgene.

5.6. Plastic test tubes: 12- x 75-mm and 17- x 100-mm.

6. Reagents

NOTE: Use plastic bottles and Nalgene volumetric flasks for preparation and storage of all reagents and standards.

6.1. Oxalic acid solution. Dissolve 50 g of oxalic acid in approximately 450 mL of ASTM Type I water and bring to 500 mL with ASTM Type I water. Store in a plastic bottle.

6.2. Sulfuric acid (concentrated, reagent-grade).

6.3. Ammonium molybdate reagent. Dissolve 20 g of ammonium molybdate in approximately 400 mL of ASTM Type I water. Add 8 mL of concentrated H_2SO_4 and bring to 500 mL with ASTM Type I water. Store in a plastic bottle at 40°C. Prepare fresh each month. Discard reagent if a precipitate or blue color is observed.

6.4. ANSA reagent. Dissolve 2 g of sodium sulfite in approximately 80 mL of ASTM Type I water. Add 0.25 g of 1-amino-2-naphthol-4-sulfonic acid (Kodak #360). Dissolve and dilute to 100 mL with ASTM Type I water.

6.5. Reducing agent. Dissolve 15 g of sodium bisulfite in approximately 250 mL of ASTM Type I water and dilute to 300 mL with ASTM Type I water.

6.6. Mixed reagent. Mix ANSA reagent and reducing agent in a plastic bottle. Add 4 mL of glycerol. Avoid light. Store under refrigeration. Discard reagent when it becomes dark in color or after 6 months. Tubing that carries this reagent clogs easily and needs frequent changing.

6.7. Degas all reagent solutions with He.

7. Calibration and Standards

7.1. SiO_2 stock standard A (1000 mg/L). Dissolve 4.7298 g of sodium metasilicate nonahydrate ($Na_2SiO_2 \bullet 9H_2O$) in approximately 800 mL of ASTM Type I water and dilute to 1 L. Store in a plastic bottle. A commercially prepared standard from Fisher Scientific or HACH may be used.

7.2. Working standards. Pipette the following volumes of stock standard A into 100-mL Nalgene volumetric flasks. Dilute to volume with ASTM Type I water.

Stock Standard A (mL)	SiO_2 (mg/L)
0.5	5
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100

8. Procedure

8.1. Connect sample loop, sampler, waste, reaction module, and carrier lines to valve. Place pump feed lines in reagents. Tighten pump cartridges. Place waste lines in waste container. Insert 820-nm filter in detector.

8.2. Turn all power switches on.

8.3. At prompt from system computer, download SiO_2 High method from menu on master computer.

8.4. Turn on pump and run at speed 35.

8.5. Check for proper flow and look for leaks.

8.6. Check for steady baseline.

8.7. Initiating a run. Select SAMPLES from MAIN MENU. Select TRAY DEFINITION and SUBMIT. Select EDIT and IDENTIFICATION. Enter QC and sample identification for the run including 10% QCs, duplicates, and spikes. Follow last entry with "..." to end. Select SUBMIT and SUBMIT CURRENT TRAY. Printer switch should be on CHART RECORDER.

8.8. Calibration. Fill large plastic tubes with standards and smaller tubes with samples. Load sampler cartridges. Check for shape of peaks on monitor. At completion of standard peaks and approval of the calibration, the tray is processed automatically. (See software manual for procedure to manually approve the calibration.)

8.9. Results. Select RESULTS/APPROVAL from MAIN MENU. Select CALIBRATION TRAY and CALIBRATION GRAPHS and STATS to view the calibration. Select SAMPLE TRAY and REPORTS for report of tray. Switch to MASTER PRINTER. Print report.

8.10. Rinse reagent feed lines and place in ASTM Type I water. Pump to flush system at least 10 min. Remove lines from water and pump lines dry. Turn all power off. Loosen pump cartridges then remove reagent lines and sample loop.

8.11. System notes.

8.11.1. Timing - automatic.
Pump speed 35.
Cycle period 65 s.
Inject to start of peak period 30 s.
Inject to end of peak period 92 s.

8.11.2. Carrier is helium - degassed H_2O.

8.11.3. Manifold tubing is 0.8-mm (0.032-in.) i.d.

8.11.4. Reagent lines are 0.03-in. i.d.

9. Calculations

9.1. Samples are spiked by adding 1.0 mL of standard A to a 50-mL volumetric flask and bringing to volume with sample. Spike concentration of SiO_2 added is 20 mg/L.

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.2. Percent recovery should be between 85% and 115%. If recovery is outside acceptable limits, check open and blind QC results and duplicate precision. If these are within specifications, report value with comment "spike recovery outside acceptable limits." Check duplicates, QCs, check standards, and blanks and report the result if these are okay for the run. Troubleshoot if spikes are consistently out.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where $\%R$ = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. No hazardous waste is generated by this procedure.

11. Source Materials

11.1. QuikChem Method No. 10-114-27-1-B (Lachat Instruments, Milwaukee, Wisconsin, 1991).

11.2. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 425C (American Public Health Association, Washington, DC, 1985).

11.3. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 370.1 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

FLUORIDE IN WATER AND WASTEWATER—FLOW INJECTION*

Analyte: Fluoride	**Method No.:** WI460
Matrix: Water and wastewater	**Range:** 0.1 - 5.0 mg/L
Procedure: Flow injection with ion-selective electrode on Lachat QuikChem AE	**Detection Limit:** 0.10 mg/L **Accuracy and Precision:** 100% ± 3% RSD
Effective Date: 04/21/92	**Author:** Kathleen Straw

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. A buffer is added to both standards and samples to adjust ionic strength to a uniformly high value and to complex interfering metals.

1.2. Fluoride is determined potentiometrically using a combination fluoride electrode and the Lachat QuikChem Flow Injection Analyzer. The fluoride electrode consists of lanthanum fluoride crystal across which a potential is developed by fluoride ions. The reference cell is a $Ag/AgCl/Cl^-$ cell. The reference junction is of the annular liquid-junction type and encloses the fluoride-sensitive crystal.

2. Accuracy and Precision

2.1. The determination of fluoride in 25 Environmental Protection Agency (EPA) quality control (QC) samples (1.00 ± 0.05 mg/L) over a period of 16 months had a mean of 1.0 mg/L and a relative standard deviation (RSD) of 3%.

2.2. Thirty samples spiked with 1.0 mg/L of F^- over a period of 16 months resulted in an average recovery of 102% and an RSD of 5%. The percent recovery ranged from 86% to 110%.

3. Interferences

3.1. At high pH, hydroxide interferes with electrode response when $[OH] > 0.1\ [F^-]$.

*This procedure has been substantially revised. Therefore, individual changes are not highlighted as they are in other revised procedures.

3.2. At pH <5 the hydrogen ion complexes the fluoride ion.

3.3. The polyvalent cations Si^{+4}, Al^{+3}, and Fe^{+3} interfere by forming complexes with fluoride. CDTA (1,2-cyclohexylenediaminetetraacetic acid) is added to preferentially complex these cations and eliminate this interference when these concentrations do not exceed 3.0 mg of Al^{+3} or 20 mg of Fe^{+3}/L.

4. Collection and Storage of Samples

4.1. Collect samples in polyethylene bottles. No additional preservation is necessary.

4.2. Complete analysis within 28 days.

5. Apparatus

5.1. Lachat QuikChem AE Flow Injection Analyzer System (Lachat Instruments, Milwaukee, WI 53218-1239).

5.1.1. Random access sampler (A11120).

5.1.2. Reagent pump (A22100).

5.1.3. Sample processing module (A24001).

5.1.4. Reaction module for QuikChem method #10-109-12-2-A.

5.1.5. Fluoride ion-selective electrode (ISE) detector (24914).

5.1.6. ISE for fluoride (13304).

5.1.7. ISE flow cell (50948).

5.1.8. IBM PS/2 Model #30-286 computer with IBM color monitor (#8512-001).

5.2. Pipettes: class A, volumetric, various sizes.

5.3. Flasks: class A, volumetric, various sizes, Nalgene.

5.4. Pipette: 1000-μL, Eppendorf, disposable tips.

5.5. Bottles: 1-L, polyethylene, clear, opaque.

5.6. Beakers: 50-mL, disposable, polyethylene.

6. Reagents

NOTE: Prepare and store all reagents in polyethylene to avoid contamination from borosilicate glass. Use distilled deionized water. De-gas all reagents with helium for 1 min.

6.1. Sodium hydroxide (5 N). Dissolve 200 g of NaOH in distilled water. Cool and dilute to 1 L.

6.2. Stock A fluoride standard (100 mg/L). Dissolve 0.221 g of anhydrous sodium fluoride (NaF) in distilled water and dilute to 1 L or dilute 10.0 mL of Banco 1000-mg F^-/L standard to 100 mL with distilled H_2O. Store in a chemical-resistant polyethylene bottle. Or use fluoride standard solution (100 ± 1 mg/L as F), catalog no. 232-49, Hach Co., Loveland, Colorado.

6.3. Total ionic strength adjustment buffer (TISAB). Add 57 mL of glacial acetic acid, 30 g of NaOH, 58.0 g of NaCl, and 4.0 g of CDTA to 500 mL of distilled deionized water in a 1-L beaker. Stir to partially dissolve. Adjust pH to 5.0 - 5.5 range using 5 N NaOH (approximately 25 mL). Transfer solution to a 1-L volumetric flask, add 0.5 mL of stock standard (100 mg/L), dilute to volume, and mix. Store in polyethylene.

6.4. Carrier solution (1.0 mg/L of F). Add 10 mL of stock standard (100 mg/L) to 1-L volumetric flask. Bring to volume and mix well.

6.5. Electrode conditioning solution. Mix together in 1-L container 500 mL of TISAB buffer and 500 mL of carrier solution.

7. Calibration and Standards

7.1. Working stock standard B (5.0 mg of F^-/L). In a 1-L volumetric flask, dilute 50.0 mL of stock standard A to volume with distilled deionized water and mix.

7.2. Calibration standards. Add the following volumes of standard B to 250-mL polyethylene flasks; make up to volume with distilled deionized water and mix:

Stock Standard B (mL)	Conc. (mg F^-/L)
250.0	5.00
100.0	2.00
50.0	1.00
25.0	0.50
10.0	0.20
5.0	0.10

8. Procedure

8.1. Preparation of fluoride electrode.

NOTE: This procedure applies only to new electrodes or electrodes that have been stored dry.

8.1.1. Assembly: Remove the protective boot from the end of the electrode and put a couple of milliliters of filling solution (Orion no. 90-00-01) into the electrode through the fill hole in the body. Tilt and shake the electrode to wet the green O-ring at the top of the electrode. Unscrew the electrode cap about three turns then push the body into the cap and allow the solution to drain out of the electrode. Retighten the electrode cap then fill the electrode with filling solution to the level of the fill hole. Suspend the electrode in a beaker containing electrode conditioning solution and allow to equilibrate for at least 2 h, or preferably overnight.

8.1.2. Prepare the following to check the electrode:

Test solution 1. 10.0 mg of F^-/L.
To a 100-mL container, add 5.0 mL of standard A, 50.0 mL of TISAB buffer, and 45.0 mL of water. Shake or stir to mix thoroughly.

Test solution 2. 1.00 mg of F^-/L.
To a 100-mL container, add 0.50 mL of standard A, 50.0 mL of TISAB buffer, and 49.5 mL of water. Shake or stir to mix thoroughly.

Test solution 3. 0.00 mg of F^-/L.
To a 100-mL container, add 50.0 mL of reagent A and 50.0 mL of distilled deionized water. Shake or stir to mix thoroughly.

8.1.3. Determine the slope of the electrode.

Attach the conditioned electrode to a digital volt meter using an appropriate patch cord. Set the meter to read DCmV. (Beckman pH meter set to mV). Place the electrode tip in test solution 2. When the meter reading is stable for at least 5 s, record the reading in mV. This is reading A. Rinse the electrode briefly and place it in test solution 1. When the meter reading is stable for at least 5 s, record the reading in mV. This is reading B. Rinse the electrode and place in test solution 3. This is reading C. Calculate the differences (in mV) between reading A and reading B (A-B) and between reading C and reading A (C-A). If both differences are larger than 45 mV, the electrode passes the test and should perform well. If the electrode fails, polish the sensing surface with fluoride toothpaste, rinse thoroughly, and soak overnight in electrode conditioning solution before retesting.

8.2. Connect the electrode cable to the fluoride detector head. Connect the ground. Fill the electrode with filling solution to level of opening. Finger-tighten the electrode into the flow cell.

8.3. Connect the sample loop, sampler, waste, reaction module, and carrier lines to the valve. Place the pump feed lines in the reagents. Tighten the pump cartridges.

8.4. Turn all power switches on.

8.5. At the prompt from the system computer, download FNEW method (Channel #2) from the menu on the master computer.

8.6. Turn on the pump and run at speed 35.

8.7. Check for proper flow and look for leaks.

8.8. Check for steady baseline approximately midscale.

8.9. Initiating a run.

Select SAMPLES from MAIN MENU. Select TRAY DEFINITION and SUBMIT. Select EDIT and IDENTIFICATION. Enter QC and sample identification for the run including 10% QCs, duplicates, and spikes. Follow last entry with "..." to end. Select SUBMIT and SUBMIT CURRENT TRAY. Printer switch should be on CHART RECORDER.

8.10. Calibration.

Check for shape of peaks on monitor. At completion of standard peaks and approval of the calibration, the tray is processed automatically. (See software manual for procedure to manually approve the calibration.)

8.11. Results.

Select RESULTS/APPROVAL from MAIN MENU. Select CALIBRATION TRAY and CALIBRATION GRAPHS and STATS to view the calibration. Select SAMPLE TRAY and REPORTS for report of tray. Switch to MASTER PRINTER. Print the report.

8.12. Rinse the reagent feed lines and place them in distilled deionized water. Pump to flush the system at least 10 min. Remove the lines from the water and pump the lines dry. Turn all power off. Loosen the pump cartridges and remove the reagent lines and sample loop. Remove the electrode, disconnect the ISE cable, and store the electrode in the flask containing conditioning solution.

8.13. System settings.

Parameter, evaluation, signal processing:

System unit signal processing scheme, direct voltage, ADC setting no. 1.

Parameter, presentation, data window:

Top scale response:	1.50
Bottom scale response:	1.00

Parameter, timing, mode:

MANUAL timing:	Y

Parameter, timing, periods:

Cycle period:	60.00 s
Transition to LOAD:	18.00 s
Transition to INJECT:	30.00 s
Leading baseline start:	7.00 s
Leading baseline width:	2.00 s
Peak start:	14.00 s
Peak width:	15.00 s
Trailing baseline start:	67.00 s
Trailing baseline width:	2.00 s

NOTE: As in the EPA Method 340.2, the sample is automatically mixed on the manifold with an equal volume of buffer. The standard curve is nonlinear and therefore point-to-point segmentation is used in the data reduction. To increase baseline stability and decrease the response time of the electrode, the carrier contains 1 mg of F/L. This results in inverted peaks for standards 0.50, 0.20, and 0.10. The characteristics of the fluoride electrode change as the electrode ages. A 60-s cycle is typical for a new electrode. As the electrode ages, the response time lengthens to compensate for this. The time required for the electrode response to return to baseline between injections of the high standards is the minimum cycle time that should be used. If the recovered concentrations for the check standards are consistently high, the cycle period needs to be increased. The output of the electrode in the carrier stream (baseline voltage) changes with the age of the electrode. After several months of operation, the data window will need to be changed so that the trace for the baseline is at the center of the screen.

9. Calculations

9.1. Samples are spiked by adding 1.0 mL of standard A to a 50-mL volumetric flask and bringing to volume with sample. Spike concentration of F^- added is 1.0 mg/L.

$$R = C_s - C \quad ,$$

where R = amount recovered (mg/L),
C_s = concentration of spiked sample (mg/L), and
C = concentration of unspiked sample (mg/L).

9.2. Percent recovery should be between 85% and 115%.

$$\%R = \frac{R \times 100}{A} \quad ,$$

where $\%R$ = percent recovery,
R = amount recovered (mg/L), and
A = amount added (mg/L).

10. Proper Waste Disposal Practices

10.1. No hazardous waste is generated by this procedure.

11. Source Materials

11.1. American Public Health Association, American Waterworks Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, 16th ed., Method 413B (American Public Health Association, Washington, DC, 1985).

11.2. Environmental Monitoring and Support Laboratory, *Methods for Chemical Analysis of Water and Waste*, Method 340.2 (Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio, 1983).

11.3 QuikChem Method 10-109-12-2-A (Lachat Instruments, Milwaukee, Wisconsin, 1992).

INORGANIC TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)

Analyte: Trace metals	**Method No.:** WI650
Matrix: Sludges, soils, and RCRA wastes	
Procedure: Acid leach to extract metals	
Effective Date: 04/01/87	**Authors:** Mary Carol Williams Daniel J. Gerth

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 10 of this procedure and Source Materials 11.3 and 11.4 for proper waste disposal practices.

1. Principle of Method

1.1. The toxicity characteristic leaching procedure (TCLP) is designed to determine the mobility of contaminants present in liquid, solid, and multiphasic wastes.

1.2. For liquid wastes (i.e., those containing <0.5% solid material), the waste, after filtration through a 0.6- to 0.8-μm glass-fiber filter, is defined as the TCLP extract.

1.3. For solid wastes or wastes containing significant amounts of solid material, the particle size of the waste is reduced (if necessary), and the liquid phase, if any, is separated from the solid phase and stored at 4°C for later analysis. The solid phase is extracted with 20 times its weight of extraction fluid. The choice of extraction fluid employed depends on the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6- to 0.8-μm glass-fiber filter.

1.4. If a total analysis of the waste demonstrates that individual contaminants are not present or that they are present at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

1.5. If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste and the liquid extract are combined and analyzed. If incompatible, the liquids are analyzed separately, and the results are mathematically combined to yield a volume-weighted average concentration.

1.6. The maximum concentrations of contaminants for characteristics of toxicity are as follows:

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

2. Accuracy and Precision

2.1. A well-characterized matrix is not available to measure either accuracy or precision. Spike recovery is variable depending on the absorptive characteristics of the matrix.

3. Interferences

3.1. Chloride interferes, causing low recoveries for Cr, As, Se, and Ag.

3.2. Samples can be extremely complex and can have a multitude of unidentified, continuously variable interferences.

4. Handling and Storage of Samples

4.1. Preservatives must NOT be added to samples.

4.2. Sludges from TA-50 or TA-57 must be handled in a glove box. The handler must wear an anti-C lab coat, safety glasses, and rubber gloves. Weighing and dissolution must be completed in a glove box.

4.3. TCLP extracts should be preserved with nitric acid at a pH <2, prepared for analysis, and analyzed as soon as possible following extraction.

5. Apparatus

5.1. Glove box: with balance, for use with radioactive samples, if necessary.

5.2. Extraction vessel: 2-L bottle, borosilicate glass or plastic.

5.3. Magnetic stirring bar: Teflon-coated.

5.4. Magnetic stirrer: heavy duty.

5.5. Agitation apparatus: capable of rotating the extraction vessel end over end at 30 ± 2 rpm, from Associated Design and Manufacturing Company, Alexandria, Virginia, or equivalent to meet Environmental Protection Agency (EPA) requirements as described in "Test Methods for Evaluating Solid Wastes" (40 CFR 261).

5.6. Pressure filter holder: Fisher Model 09-753-25K or equivalent to meet EPA requirements as described in "Test Methods for Evaluating Solid Wastes" (40 CFR 261).

5.7. Filter media: 0.7-μm, Whatman GFF, Whatman Laboratory Products, Clifton, New Jersey, or equivalent to meet EPA requirements as described in "Test Methods for Evaluating Solid Wastes" (40 CFR 261).

5.8. Polyethylene bottle: 250-mL.

5.9. pH meter: calibrated in accordance with manufacturer's specifications.

5.10. Hot plate.

5.11. Laboratory balance: any balance accurate to ±0.01 g.

6. Reagents

6.1. ASTM Type I water.

6.2. Hydrochloric acid, 1.0 N: prepare from American Chemical Society (ACS) reagent-grade (87 mL/L).

6.3. Nitric acid, 1.0 N: prepare from ACS reagent-grade (60 mL/L).

6.4. Sodium hydroxide, 10 N.

6.5. Acetic acid: glacial, ACS reagent-grade.

6.6. Extraction fluid no. 1: prepare by adding 11.4 mL of glacial acetic acid to 1975 mL of ASTM Type I water. Add 12.9 mL of 10 N NaOH. When correctly prepared, the pH of this fluid is 4.93 ± 0.05.

6.7. Extraction fluid number 2: prepare by adding 11.4 mL of glacial acetic acid to 1989 mL of ASTM Type I water. When correctly prepared, the pH of this fluid is 2.88 ± 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked before use to ensure that these fluids were accurately prepared.

6.8. Metal standards, 1000 mg/L stock solutions. See individual metal procedures.

6.9. Nitric acid: concentrated, reagent-grade.

6.10. Nitric acid, 1%: dilute 10 mL of concentrated nitric acid to 1000 mL with ASTM Type I water.

6.11. Spike solution: use 1000 mg/L metal standards in the nitrate or oxide form. Add 10 mL of Ag; 5 mL each of As, Cr, Pb, and Se; 1 mL of Cd; and 100 mL of Ba. Add standard solutions to approximately 100 mL 1% HNO_3. Dilute to 1000 mL with 1% HNO_3. Do not use HCl solutions, which will precipitate silver.

Element	Spike solution concentration (mg/L)	Spiked sample concentration (mg/L)
As	5	0.1
Cd	1	0.02
Cr	5	0.1
Pb	5	0.1
Se	5	0.1
Ag	5	0.1
Ba	100	10.0

7. Procedure

7.1. The preliminary TCLP evaluations are performed on representative samples of waste (minimum aliquot size of 100 g) that will not actually undergo TCLP extraction. These evaluations include preliminary determination of the percent solids of the waste; determination of whether the waste contains insignificant solids and is therefore its own extract after filtration; determination of whether the solid portion of the waste requires particle-size reduction; and determination of which extraction fluid is to be used.

7.2. Preliminary determination of percent solids. Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid can be forced by applied pressure, as described below.

7.2.1. If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids), proceed to Step 7.5.

7.2.2. If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This separation involves the filtration device described in Steps 5.6-5.7 and is outlined in Steps 7.2.3-7.2.9.

7.2.3. Weigh the filter and the container that will receive the filtrate.

7.2.4. Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.2.5. Weigh out a representative subsample of the waste (100-g minimum) and record the weight.

7.2.6. Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged before filtration. Centrifugation is to be used only as an aid to filtration. If centrifugation is used, the liquid should be decanted and filtered and the solid portion of the waste filtered through the same filtration system.

7.2.7. Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). If filtration of the waste at 4°C reduces the amount of expressed liquid below what would be expressed at room temperature, allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5 to determine the weight of the waste sample that will be filtered.

Gradually apply gentle pressure (1-10 psi) until pressurizing gas moves through the filter. If this point is not reached under 10 psi and if no additional liquid has passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10-psi, if the pressurizing gas has not moved through the filter and if no additional liquid has passed through the filter in any 2-min interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter or when liquid flow has ceased at 50 psi (i.e., filtration does not produce any additional filtrate within any 2-min period), filtration is stopped.

NOTE: Instantaneous application of high pressure can degrade the glass-fiber filter and may cause premature plugging.

7.2.8. The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. But even after applying pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material in the filtration device is defined as a solid. The original filter is **NOT** to be replaced with a fresh filter under any circumstances. Only one filter is to be used.

7.2.9. Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.2.3) from the total weight of the filtrate-filled container. The weight of the solid phase of the waste sample is determined by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.2.5.

7.2.10. Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\%S = \frac{W_S \times 100}{W_T} ,$$

where %S = percent solids,
W_S = weight of solid, and
W_T = total weight of waste.

7.3. Determination of whether waste is liquid or has insignificant amounts of solid material. If the sample obviously has a significant amount of solid material, the solid phase must be extracted. Proceed to Step 7.4 to determine if the waste requires particle-size reduction, and reduce particle size if necessary. Determine whether the waste is liquid or has insignificant amounts of solid material, which need not undergo extraction, as follows:

7.3.1. Remove the solid phase and filter from the filtration apparatus.

7.3.2. Dry the filter and solid phase at 100 ± 20°C until two successive weighings yield the same value within ±1%. Record the final weight.

NOTE: Caution should be taken to ensure that the solid will not flash upon heating. The drying oven should be vented to a hood or appropriate device.

7.3.3. Calculate the percent dry solids as follows:

$$\%D_s = \frac{(W_{wf} - W_f) \times 100}{W_i} ,$$

where: $\%D_s$ = percent dry solids,
W_{wf} = weight of dry waste and filter,
W_f = tared weight of filter, and
W_i = initial weight of sample.

7.3.4. If the percent dry solids is <0.5%, the waste after filtration is defined as the TCLP extract. If the percent dry solids is ≥0.5% and TCLP is to be performed, return to the beginning of this section (Step 7.1) with a new representative waste sample, so that it can be determined if particle-size reduction is necessary (Step 7.4) and so that the appropriate extraction fluid may be determined (Step 7.5) on a fresh portion of the solid phase of the waste.

7.4. Determination of whether the wastes require particle-size reduction (particle size is reduced during this step). Using the solid portion of the waste, evaluate the solid for particle size. If the solid has a surface area per gram ≥3.1 cm^2 or is <1 cm in its smallest dimension (i.e., is capable of passing through a 9.5-mm [0.375-in.] standard sieve), particle-size reduction is not required (proceed to Step 7.5). If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

7.5. Determination of appropriate extraction fluid. If the solid content is ≥0.5% of the waste and if TCLP extraction is to be done (Section 8), determine the appropriate fluid (Steps 6.6-6.7) to use as follows.

7.5.1. Weigh out a small subsample of the solid phase of the waste, reduce the particle size (if necessary) to approximately 1-cm-diam or less, and transfer 5.0 g of the solid phase of the waste to a 250-mL (or larger) beaker or Erlenmeyer flask.

7.5.2. Add 96.5 mL of reagent water (ASTM Type I) to the beaker, cover with a watch glass, and stir vigorously for 5 min with a magnetic stirrer. Measure and record the pH. If the pH is <5.0, extraction fluid No. 2 is used. Proceed to Section 8.

7.5.3. If the pH from Step 7.5.2 is >5.0, add 3.5 mL 1.0 N HCl, slurry briefly, cover with a watch glass, heat to 50°C, and hold at 50°C for 10 min.

7.5.4. Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid No. 1. If the pH is >5.0, use extraction fluid No. 2. Proceed to Section 8.

7.6. The sample of waste used in this step must **NOT** be used any further. Use a new sample of the waste for extractions in Steps 8 and 9.

8. Extraction Procedure

8.1. Although a sample of at least 100 g (solid and liquid phases) is required, a larger sample may be more appropriate, depending on the solids content of the waste sample (percent solids, see Step 7.2) and whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid. Enough solids should be generated for extraction so that the volume of TCLP extract will be sufficient to support all the determinations required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all the determinations required, it is recommended that more than one extraction be performed and that the extracts from each extraction be combined and then aliquoted for analysis.

8.2. If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Step 7.2), weigh out a representative subsample of the waste (100-g minimum) and proceed to Step 8.10.

8.3. If the sample is liquid or multiphasic, liquid/solid separation is required. This separation involves filtration and is outlined in Steps 8.4 to 8.9 below.

8.4. Weigh the container that will receive the filtrate.

8.5. Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure it. Acid-wash the filter.

8.6. Weigh out a representative subsample of the waste (100-g minimum) and record the weight. If the waste was shown to contain <0.5% dry solids (Step 7.3), the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all the determinations required of the TCLP extract. For wastes containing >0.5% dry solids (Steps 7.2 or 7.3), use the percent solids information obtained in Step 7.2 to determine the optimum sample size (100-g minimum) for filtration. Enough solids should be generated after filtration to support the determinations to be performed on the TCLP extract.

8.7. Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged before filtration. Centrifugation is to be used only as an aid to filtration. If centrifugation is used, the liquid should be decanted and filtered and the solid portion of the waste filtered through the same filtration system.

8.8. Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder. If filtration of the waste at 4°C reduces the amount of expressed liquid below what would be expressed at room temperature, allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.6, to determine the weight of the waste sample that will be filtered.

Gradually apply gentle pressure (1-10 psi) until pressurizing gas moves through the filter. If this point is not reached below 10 psi and if no additional liquid has passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase, if the pressurizing gas has not moved through the filter and if no additional liquid has passed through the filter in any 2-min interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter or when the liquid flow has ceased at 50 psi (i.e., filtration does not produce any additional filtrate within a 2-min period), filtration is stopped.

NOTE: Instantaneous application of high pressure can degrade the glass-fiber filter and may cause premature plugging.

8.9. The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 8.14) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. But even after applying vacuum or pressure filtration, as outlined in Step 8.8, this material may not filter. If this is the case, the material in the filtration device is defined as a solid and is carried through the extraction as a solid. The original filter is not to be replaced with a fresh filter under any circumstances. Only one filter is to be used.

8.10. If the waste contains <0.5% dry solids (see Step 7.3), proceed to Step 8.14. If the waste contains >0.5% dry solids (see Step 7.2 or 7.3) and if particle-size reduction of the solid was needed in Step 7.4, proceed to Step 8.11. If particle-size reduction was not required in Step 7.4, quantitatively transfer the solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase, and proceed to Step 8.12.

8.11. The solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Step 7.4. When the surface area or particle size has been appropriately altered,

quantitatively transfer the solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

NOTE: The waste should be sieved only through a Teflon-coated sieve, to avoid possible contamination of the sample. Surface area requirements are meant for filamentous (e.g., paper or cloth) and similar waste materials. Actual measurement of surface area is not recommended.

8.12. Determine the amount of extraction fluid to add to the extractor vessel as follows:

Weight of extraction fluid = 0.5 × % solids × weight of waste filtered.

Slowly add this amount of appropriate extraction fluid (see Step 7.5) to the extractor vessel. Close the extractor bottle tightly (Teflon tape can be used to ensure a tight seal), secure it in the rotary extractor device, and rotate it at 30 ± 2 rpm for 18 ± 2 h. Ambient temperature (i.e., temperature of room in which extraction is to take place) must be maintained at 22 ± 3°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., lime or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be opened periodically (e.g., after 15 min, 30 min, and 1 h) and vented into a hood.

8.13. Following the extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass-fiber filter, as outlined in Step 8.8. For final filtration of the TCLP extract, the filter may be changed, if necessary, to facilitate filtration. Filter(s) must be acid-washed if the mobility of metals is being evaluated.

8.14. The TCLP extract is prepared as follows:

8.14.1. If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.13 is defined as the TCLP extract. Proceed to Step 8.15.

8.14.2. If compatible (i.e., multiple phases will not result on combination), the filtered liquid resulting from Step 8.13 is combined with the initial liquid phase of the waste obtained in Step 8.8. This combined liquid is defined as the TCLP extract. Proceed to Step 8.15.

8.14.3. If the initial liquid phase of the waste obtained from Step 8.8 is not or may not be compatible with the filtered liquid resulting from Step 8.13, these liquids are not combined. These liquids, collectively defined as the

TCLP extract, are analyzed separately and the results are combined mathematically. Proceed to Step 8.15.

8.15. Following collection of the TCLP extract, record the pH of the extract. The extract should be immediately aliquoted for analysis and properly preserved (metals aliquots must be acidified with concentrated nitric acid to pH <2). The TCLP extract must be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals other than mercury must be acid digested.

8.16. The contaminant concentrations in the TCLP extract are compared with the thresholds identified in the appropriate regulations. Refer to Source Material 11.1 for quality assurance requirements.

9. Calculations

9.1. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ±0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final analyte concentration} = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2} ,$$

where V_1 = the volume of the first phase (L),
C_1 = the concentration of the contaminant of concern in the first phase (mg/L),
V_2 = the volume of the second phase (L), and
C_2 = the concentration of the contaminant of concern in the second phase (mg/L).

Chromium concentrations must be interpreted differently. A waste containing chromium will be determined to be toxic if (1) the waste extract has an initial pH of <7 and contains more than 5 mg/L of hexavalent chromium in the resulting extract, or (2) the waste extract has an initial pH >7 and a final pH >7 and contains more than 5 mg/L of hexavalent chromium in the extract, or (3) the waste extract has an initial pH >7 and a final pH <7 and contains more than 5 mg/L of total chromium, unless the chromium is trivalent. To determine whether the chromium is trivalent, the sample must be processed according to an alkaline digestion method (Method 3060) and analyzed for hexavalent chromium (Methods 7195, 7196, or 7197). (Refer to SW-846 Manual, Source Material 11.1.)

9.2. Calculation for standard additions:

$$C = \frac{D \times R_u \times C_s}{R_u - R_s} ,$$

where C = concentration of unknown,
D = dilution of both standard and unknown (must be the same for each),
R_u = instrument reading of unknown,
C_s = concentration of standard added, and
R_s = instrument reading of unknown plus standard.

10. Proper Waste Disposal Practices

10.1. Soil-water slurry.

10.1.1. The TCLP waste consists of approximately 1500 mL of a slurry that remains after filtering the sample for TCLP analysis.

10.1.2. If, after analysis, the sample is found to be below the levels of concern for the TCLP analytes, dispose of the liquid portion of the sample in a sink approved for the disposal of inorganic acids and bases. Dispose of the solid portion of the sample as ordinary laboratory trash.

10.1.2.1. Concern levels:

Cd, Se,	>	1 ppm
Ag, As, Cr, Pb	>	5 ppm
Ba	>	100 ppm

10.1.3. If, after analysis, the sample is found to be above the level of concern for any of the TCLP analytes, accumulate the slurry in a coated glass bottle in a secondary containment tray.

10.1.3.1. Label the bottle with a hazardous waste label indicating its use for the TCLP waste samples.

10.1.3.2. When the bottle is full, keep it in the secondary containment tray pending pickup by Waste Management (CST-7).

10.2. Waste pickup.

10.2.1. When the waste bottle is full, request CST-7 to pick it up by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form describing the waste is referenced on the CWDR.

10.2.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

11. Source Materials

11.1. *Test Methods for Evaluating Solid Waste, SW-846* (Office of Solid Waste and Emergency Response, Washington, D.C., 1982).

11.2. *Federal Register*, Vol. 51, No. 216, pp. 40643-40652.

11.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

11.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒). Where a section heading is marked, the entire section has been revised.

TRACE METAL DIGESTION — SLUDGE

Analyte: Ag, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn	**Method No.:** WI700
Matrix: Sludge	
Procedure: Acid digestion and atomic absorption spectrophotometry	**Accuracy and Precision:** See Sec. 2
Effective Date: 09/03/85 to 01/03/94	**Author:** Mary Carol Williams

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment.

1. Principle of Method

1.1. Organic metal complexes are decomposed by the action of hot nitric and hydrofluoric acids at elevated pressure (2 atm). After dilution and filtration, acidic solutions may be measured by atomic absorption spectrophotometry (AAS), Method No. WI100. Alternate instrumental techniques include inductively coupled plasma mass spectrometry (ICPMS), Method No. EI360, or inductively coupled plasma atomic emission spectrometry (ICPAES), Method No. EI370.

2. Accuracy and Precision

2.1. The mean and standard deviations (N = 5 replicate digestions) for various analytes are listed below.

Element	Units	Mean	±	Std. Dev.	Accepted Value
		Atomic Absorption Analyses			
Ag	mg/kg	67.2	±	6.8	80.6
As	mg/kg	3.07	±	0.22	4.3
Be	mg/kg	509	±	60	580
Cd	mg/kg	20.2	±	0.87	19.1

Element	Units	Mean	±	Std. Dev.	Accepted Value
Atomic Absorption Analyses (cont)					
Pb	mg/kg	544	±	17	526
Se	mg/kg	4.91	±	1.3	4.7
V	mg/kg	27	±	2.6	23.0
Inductively Coupled Plasma Atomic Emission Analyses					
Al	g/kg	14.1	±	0.78	13.0
Ba	g/kg	1.48	±	0.017	1.6
Cr	mg/kg	215	±	5.2	193
Cu	g/kg	1.08	±	0.026	1.01
Fe	g/kg	18.6	±	0.35	16.5
Mn	mg/kg	241	±	3.5	202
Ni	mg/kg	210	±	4.4	194
Ti	g/kg	2.29	±	0.044	2.12
Zn	g/kg	1.48	±	0.017	1.32

3. Interferences

3.1. Volatile elements such as mercury may be lost during heating. Method No. WI110 is recommended for mercury in sludges.

3.2. Arsenic forms volatile compounds with the anions present in sludge ($AsCl_3$, AsF_3, AsF_5) and may be lost during heating.

4. Apparatus

4.1. Digestion.

4.1.1. Analytical balance: capable of weighing to 0.0001 g.

4.1.2. Pressure cooker: 8-qt. with 15-lb weight.

4.1.3. Hot plate: adjustable.

4.1.4. Centrifuge tubes: 50-mL, graduated, polyethylene.

4.1.5. Funnels: disposable.

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Health and Environmental Chemistry: Analytical Techniques, Data Management, and Quality Assurance

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The page numbering convention used in this manual consists of the specific procedure number (shown at left in list below) followed by the page number for that procedure. Thus, QCI110-2 is page two of procedure QCI110. The right column in the list below gives each procedure's status or effective date.

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PREFACE

The Environment, Safety, and Health (ESH) and Chemical Science and Technology (CST) divisions are engaged in work to identify hazards to the workers and to the environment at Los Alamos National Laboratory. Decisions that must be made in these areas depend upon the availability of sound analytical data. Procedures for the measurement of the presence and concentration of substances hazardous to human health as well as an evaluation of the quality of the environment are essential to satisfactory decision making.

The analytical method evaluates the exposure of workers and the environment to toxic substances. An important tool for evaluating the accuracy of the analytical method is the blind quality control (QC) sample inserted into each analytical batch. This section of the manual is a collection of QC sample preparation methods used by the Quality Assurance and Data Management team of Analytical Services (CST-3) to monitor the routine analytical performance of environmental chemistry groups. These written methods are part of the overall QC documentation effort to support the health, safety, and environment programs of the Laboratory.

The QC preparation procedures were developed by the staff of the Quality Assurance and Data Management team and are presented in a simple and concise manner. We hope that any competent analyst will be able to use these written procedures.

ACKNOWLEDGMENTS

The encouragement, leadership, and support offered by Analytical Services (CST-3) management are appreciated. The information provided by Organic Analysis (CST-12) during the development of the organic QC preparation procedures is gratefully acknowledged. The general contributions of the following individuals in developing, evaluating, or writing the methods contained herin are formally acknowledged:

Margaret A. Gautier, Quality Assurance and Data Management Team Leader
Nancy L. Koski
William D. Moss

The section is prepared in loose-leaf form to facilitate revisions of the procedures and the inclusion of additional procedures. Requests for clarification or for help in resolving difficulties encountered while using the procedures are welcome.

Margaret A. Gautier
Editor

Quality Assurance
QC Sample Preparation Techniques

Edited by

Margaret A. Gautier

ABSTRACT

This section of the manual documents the quality control (QC) methodology used by the Los Alamos National Laboratory's environmental chemistry groups. It is part of the overall QC effort to support the health, safety, and environmental programs at the Laboratory. This section provides organic, inorganic, and radiochemistry QC sample preparation procedures used to monitor our routine analytical work. The QC preparation procedures, developed by staff within the Quality Assurance and Data Management team of Analytical Services (CST-3), have been used over several years to test their validity. QC samples prepared using these methods will fall within the calibration ranges of our analytical procedures. The QC methods use equipment and skills available in modern analytical chemistry laboratories. Precision and accuracy statements are provided for each procedure and analytical data is provided where data are available. Each procedure is presented in a simple and concise manner and includes sections on apparatus, reagent preparation, calibration methods, and data calculation formulas.

ELECTRICAL CONDUCTIVITY/RESISTIVITY OF WATER

Analyte: Conductivity/resistivity	**Method No.:** QCI105
Matrix: Water	**Accuracy and Precision:** 100 ± 0.5% RSD
Procedure: Temperature-compensated conductivity/resistivity meter	
Effective Date: 04/05/93	**Authors:** Bennie A. Martinez Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Material 9.3 for proper waste disposal practices.

1. Principle of Method

1.1. The electrical resistivity is measured in ohms per centimeter using a Horiba DS-15 temperature-compensated conductivity/resistivity meter.

1.2. The resistivity at 25°C of Type I reagent water is >18 MΩ/cm, for Type II reagent water is >1.0 MΩ/cm, and for Type III reagent water is >0.4 MΩ/cm.

1.3. For samples with low conductivity, such as deionized and distilled water, resistivity readings are more accurate than conductivity measurements.

1.4. The carbon dioxide normally present in the air can drastically change the resistivity of pure waters. Flow-through or in-line cells should be used to avoid contamination from the atmosphere.

2. Accuracy and Precision

2.1. The accuracy and precision are equal to the reproducibility, which is ± 0.5% relative standard deviation (RSD) on full scale.

3. Collection and Storage of Samples

3.1. Samples flow directly from the distilled or deionized water source through a flow-through electrode connected to the conductivity/resistivity meter.

3.2. Resistivity readings are taken after the sample stream has been adjusted to a proper flow rate and sufficient time has elapsed to permit temperature equilibrium.

3.3. Potassium chloride standards are stored in glass-stoppered borosilicate glass bottles. These standards have a six-month shelf life stored at 4°C.

4. Apparatus

4.1. Horiba DS-15 conductivity/resistivity meter with 0.1 cell constant flow-through electrode.

4.2. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.3. Desiccator.

4.4. Spatula.

4.5. Bottles: reagent, borosilicate glass.

4.6. Wash bottles: polyethylene.

4.7. Beakers: 100-, 250-, and 600-mL, glass.

4.8. Ice for ice water bath.

4.9. Volumetric flasks: 250- and 1000-mL, class A, glass.

4.10. Volumetric pipette: 10-mL, class A, glass.

4.11. Hot plate.

4.12. Clamps: hose.

4.13. Drying oven capable of reaching and sustaining a temperature of at least 105°C.

4.14. Tissue wipes.

4.15. Tubing: Teflon.

4.16. Weighing dish: small, polyethylene.

4.17. Electrical insulating mat to fit under meter.

5. Reagents

5.1. Potassium chloride (analytical reagent grade).

5.2. Conductivity calibration standard, National Institute of Standards and Technology, approximately 10 μs/cm.

5.3. Water (18 MΩ/cm or greater resistivity, specified in document ASTM D1193-91 as ASTM Type I water and referred to as reagent water in this procedure).

6. Calibration and Standards

6.1. Prepare a 0.01 N potassium chloride stock solution.

6.1.1. Tare a 100-mL glass beaker on the balance.

6.1.2. Weigh approximately 0.5 g of analytical-grade KCl into the glass beaker.

6.1.3. Place the beaker and KCl into a drying oven.

6.1.4. Dry the KCl for 2 h at 105°C.

6.1.5. Remove the beaker and KCl from the oven and cool it in a desiccator.

6.1.6. Tare a small polyethylene weighing dish.

6.1.7. Accurately weigh 186 ± 1 mg of the dried KCl into the weighing dish.

6.1.8. Use reagent water to quantitatively rinse the KCl from the weighing dish into a 250-mL volumetric flask and to dilute the solution to volume. Mix by inversion.

6.1.9. Transfer the stock solution into a reagent bottle for storage. This stock solution has a six-month shelf life stored at 4°C.

6.2. Prepare a 0.0001 N potassium chloride standard reference solution.

6.2.1. Transfer 10 mL of 0.01 N KCl stock solution into a 1000-mL volumetric flask using a 10-mL volumetric pipette.

6.2.2. Dilute the standard solution to volume with reagent water. Mix by inversion.

6.2.3. Transfer the standard solution into a reagent bottle for storage. This standard has a six-month shelf life stored at 4°C.

6.3. Set the cell constant of the electrode.

6.3.1. The first time the meter or an electrode is used the cell constant value should be entered into the conductivity/resistivity meter memory.

6.3.2. The cell constant value is marked on the base of the electrode.

6.3.3. Enter the cell constant value.

6.3.3.1. Plug the conductivity/resistivity meter AC adaptor into the wall socket.

6.3.3.2. Press the **POWER** button to turn on the unit.

6.3.3.3. Press the **FUNCTION** key.

6.3.3.4. Press the **CELL CONSTANT** key.

6.3.3.5. Enter the cell constant value using the numeric keys.

6.3.3.6. Press the **ENTER** key.

6.3.3.7. Press the **FUNCTION** key to deactivate the keyboard.

6.3.3.8. Press the **POWER** button to turn the meter off.

6.3.3.9. Unplug the meter AC adaptor from the wall socket.

6.4. Establish a temperature coefficient curve.

NOTE: The use of some type of insulation beneath the conductivity meter may help give more consistent and stable readings.

6.4.1. Temperature-conductivity characteristics of reagent water are unlike the characteristics of standard potassium chloride solution (Figs. 1 & 2). Automatic temperature conversion using a temperature coefficient curve based on water measurements more accurately reflects the temperature-conductivity characteristics of ultrapure water samples.

6.4.2. Establish a temperature coefficient curve before proceeding with sample measurements. This curve can be reused as long as the sample conditions are the same as the previous samples measured.

6.4.3. A new temperature coefficient curve must be reestablished any time the temperature range changes or when the sample to be measured exhibits different temperature-conductivity characteristics than the previous samples measured.

6.4.4. Establish a temperature coefficient curve based on a set of 2-10 pairs of temperature-conductivity readings taken at different temperatures from 0-100°C.

6.4.4.1. Collect approximately 200 mL of fresh reagent water in a clean polyethylene wash bottle.

6.4.4.2. Remove the inlet and outlet caps from the conductivity meter flow-through electrode and drain the water from the electrode.

6.4.4.3. Using the wash bottle with fresh reagent water, thoroughly rinse the electrode inlet and outlet caps.

6.4.4.4. Using the wash bottle with fresh reagent water, rinse the electrode thoroughly through the inlet hole at the top of the electrode.

6.4.4.5. Place an electrode cap over the electrode outlet found at the bottom of the electrode.

6.4.4.6. Using the wash bottle with fresh reagent water, fill the electrode up to the inlet opening through the inlet hole.

6.4.4.7. Remove the outlet cap and drain the water from the electrode.

6.4.4.8. Using the wash bottle with fresh reagent water, thoroughly rinse the electrode outlet cap.

6.4.4.9. Place an electrode cap over the electrode outlet.

6.4.4.10. Using the wash bottle with fresh reagent water, fill the electrode up to the inlet opening through the inlet hole.

6.4.4.11. Place an electrode cap over the electrode inlet to completely seal the water inside the electrode.

6.4.4.12. Plug the conductivity/resistivity meter AC adaptor into the wall socket.

6.4.4.13. Press the **POWER** button to turn on the unit.

6.4.4.14. Press the **FUNCTION** key on the meter.

6.4.4.15. Press the **AUTO-COEFFICIENT** key. The A-Curve Mode (Auto Input Multiple-Coefficient Curve Mode) symbol will start to blink, indicating the meter is waiting for input. The **DATA I.D.** number will read "0".

6.4.4.16. Prepare an ice bath in a 600-mL glass beaker.

6.4.4.17. Immerse the electrode with the water sample into the ice bath to lower the temperature to the beginning temperature of the curve. Read the temperature from the display on the meter. A typical curve for measuring at normal room temperature would begin at 15°C and end at 33°C, taking readings at 2°C increments.

6.4.4.18. When the desired beginning temperature has been reached, press the **ENTER** key to enter the temperature and conductivity values into memory. The **DATA I.D.** indicator will change from "0" to "1" to indicate that the first pair of readings has been accepted.

6.4.4.19. Lift the electrode with the water sample out of the ice bath.

6.4.4.20. Fill a 600-mL beaker to near capacity with reagent water.

6.4.4.21. Place the 600-mL beaker with reagent water on a hot plate.

6.4.4.22. Immerse the electrode containing the water sample into the 600-mL beaker with reagent water.

6.4.4.23. Slowly warm the water sample, observing the temperature reading on the display and pressing the **ENTER** key each time the water reaches the next temperature desired for the curve. A maximum of 10 pairs of data may be entered.

6.4.4.24. Press the **AUTO-COEFFICIENT** key when all the temperature-conductivity readings have been entered.

6.4.4.25. The meter will automatically compute the temperature coefficient curve and will print out the values.

6.4.4.26. Press the **FUNCTION** key to deactivate the keyboard.

6.4.4.27. Lift the electrode with the water sample out of the warm water bath.

6.4.4.28. Press the **POWER** button to turn the meter off.

6.4.4.29. Unplug the meter AC adaptor from the wall socket.

7. Procedure

NOTE: The use of some type of insulation beneath the conductivity meter may help give more consistent and stable readings.

7.1. Plug the conductivity/resistivity meter AC adaptor into the wall socket.

7.2. Press the **POWER** button to turn on the unit.

7.3. Calibrate the instrument with 0.0001 N KCl standard reference solution. If a conductivity calibration standard is available, it may be used in place of the 0.0001 N KCl standard.

7.3.1. Fill a 250-mL glass beaker 3/4 full with distilled water.

7.3.2. Warm the water in the 250-mL beaker on a hot plate to approximately 25°C.

7.3.3. Remove the inlet and outlet caps from the electrode and drain the water from the electrode.

7.3.4. Using a wash bottle with reagent water, thoroughly rinse the electrode cell through the inlet hole.

7.3.5. Pour approximately 50 mL of 0.0001 N KCl standard reference solution (or a conductivity calibration standard) into a polyethylene wash bottle.

NOTE: Discard all KCl waste into an appropriate waste container.

7.3.6. Using the wash bottle with 0.0001 N KCl, thoroughly rinse the inlet and outlet electrode caps.

7.3.7. Using the wash bottle with 0.0001 N KCl, thoroughly rinse the electrode cell through the inlet hole.

7.3.8. Place an electrode cap over the electrode outlet.

7.3.9. Using the wash bottle with 0.0001 N KCl, fill the electrode up to the inlet opening through the inlet hole.

7.3.10. Remove the outlet cap and drain the KCl from the electrode.

7.3.11. Using the wash bottle with 0.0001 N KCl, thoroughly rinse the outlet electrode cap.

7.3.12. Place an electrode cap over the electrode outlet.

7.3.13. Using the wash bottle with 0.0001 N KCl, fill the electrode up to the inlet opening through the inlet hole.

7.3.14. Place an electrode cap over the electrode inlet to completely seal the 0.0001 N KCl inside the electrode.

7.3.15. Adjust the temperature of the electrode to 25°C using the ice or warm water bath as appropriate.

7.3.16. Press the **FUNCTION** key on the meter.

7.3.17. Press the **CALIBRATION** key on the meter. The calibration symbol [CAL] will light up at the top of the display, and the main readout numerals will blink, showing the present conductivity value of the standard. The blinking indicates that the meter is waiting for input of the certified conductivity value.

7.3.18. Enter the standard solution conductivity value using the numeric keys. The conductivity value of a 0.0001 N KCl standard solution at 25°C is 14.94 μs/cm. If you are using a certified conductivity calibration standard for the calibration, use the certified conductivity value.

7.3.19. Press the **ENTER** key on the meter. When this value has been accepted, the range display will start to blink.

7.3.20. Use the **RANGE** button to select the correct range, μs/cm or mS/cm.

7.3.21. Press the **ENTER** key on the meter to input the correct range into memory. When this unit has been accepted, the **CALIBRATION** symbol [CAL] will start blinking.

7.3.22. Press the **CALIBRATION** key to begin calibration of the electrode. The **AUTO** symbol and **CELL CONST** indicator will blink during the calibration.

7.3.23. When the meter reading stabilizes, the **AUTO** symbol will go out, and the **CELL CONST** indicator will be steadily lit. The new cell constant will appear on the instrument readout display and will also be printed out. The value will be automatically entered into memory, and the conductivity/resistivity meter will operate with the new cell constant.

7.3.24. Press the **MEASURE** button to end the calibration operation and return to the main measuring display.

7.3.25. Press the **FUNCTION** key to deactivate the keyboard.

7.3.26. Press the **S/Ω** button until μs/cm appears on the display to prepare the instrument for a conductivity measurement.

NOTE: When conductivity, resistivity, or temperature readings are obtained, the meter will automatically print out the values.

7.3.27. Press the **MEASURE** button to get conductivity and temperature readings. Record the measured conductivity and temperature values.

7.3.28. Press the **S/Ω** button until MΩ/cm appears on the display to prepare the instrument for a resistivity measurement.

7.3.29. Press the **MEASURE** button to get a resistivity reading. Record the measured resistivity value.

7.3.30. Remove the two electrode caps and completely drain the KCl from the electrode.

7.3.31. Using the wash bottle with reagent water, thoroughly rinse the two electrode caps.

7.3.32. Using the wash bottle with reagent water, thoroughly rinse the electrode cell through the inlet hole.

7.3.33. Transport the conductivity/resistivity meter as described in Section 7.4.

7.4. Preparing the conductivity/resistivity meter for transport.

7.4.1. Place an electrode cap over the electrode outlet.

7.4.2. Using the wash bottle with reagent water, fill the electrode up to the inlet opening through the inlet hole.

7.4.3. Place an electrode cap over the electrode inlet to completely seal the water inside the electrode.

CAUTION: To prevent damage to the platinum electrode, the electrode cell should always contain water and be sealed with the two electrode caps whenever the meter is in transit to a water sampling station.

7.4.4. Press the **POWER** button to turn the meter off.

7.4.5. Unplug the meter AC adaptor from the wall socket.

7.4.6. Transport the conductivity/resistivity meter to a water sampling station.

7.5. Measure the conductivity and resistivity of the unknown sample.

7.5.1. Plug the meter AC adaptor into a wall socket.

7.5.2. Press the **POWER** button to turn the meter on.

7.5.3. Press the **T.C. MODE** button until the A-Curve Mode symbol appears on the display.

7.5.4. Press the **S/Ω** button until μs/cm appears on the display to prepare the instrument for a conductivity measurement.

7.5.5. Remove the two electrode caps to drain the water from the electrode.

7.5.6. Connect a piece of Teflon tubing from the water source to the inlet of the flow-through electrode.

7.5.7. Turn on the water source and flow water through the electrode.

NOTE: A small piece of tubing with a pinch clamp attached connected to the electrode outlet may be useful to regulate the water flow through the electrode.

7.5.8. Regulate the water flow through the electrode so that water fills up the cell above the two platinum electrode plates with no bubbles visible.

7.5.9. Press the **MEASURE** button to get conductivity and temperature readings. Record the measured conductivity and temperature values.

7.5.10. Press the **S/Ω** button until MΩ/cm appears on the display to prepare the instrument for a resistivity measurement.

7.5.11. Press the **MEASURE** button to get a resistivity reading. Record the measured resistivity value.

7.5.12. Turn off the water source.

7.5.13. Disconnect the Teflon tubing from the water source and from the inlet of the flow-through electrode.

7.6. Prepare the conductivity/resistivity meter for transport and continued use as described in Sections 7.4 and 7.5.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Accumulate liquid waste containing hazardous contaminants, such as solutions of trace metals, in a coated glass bottle in a secondary containment tray and keep segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

8.1.2. Label the bottle with a hazardous waste label and a label indicating its use for trace-metal waste.

8.1.3. Open the bottle only for the period of time necessary to add waste.

8.1.4. Cap the bottle when full, and keep it in the secondary containment tray pending pickup by Waste Management (CST-7).

8.1.5. Label a new bottle for future use.

8.2. Waste pickup.

8.2.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

8.2.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

9. Source Materials

9.1. A. E. Greenberg, L. S. Clesceri, and A. D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 18th ed. (American Public Health Association, Washington DC, 1992).

9.2. *Horiba Conductivity Meters: DS-10 Series Instruction Manual* (Horiba Instruments, Inc., Irvine, California, 1989).

9.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.4. *Hach Water Analysis Handbook* (Hach Company, Loveland, Colorado, 1992), pp. 268–270.

9.5. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45–47.

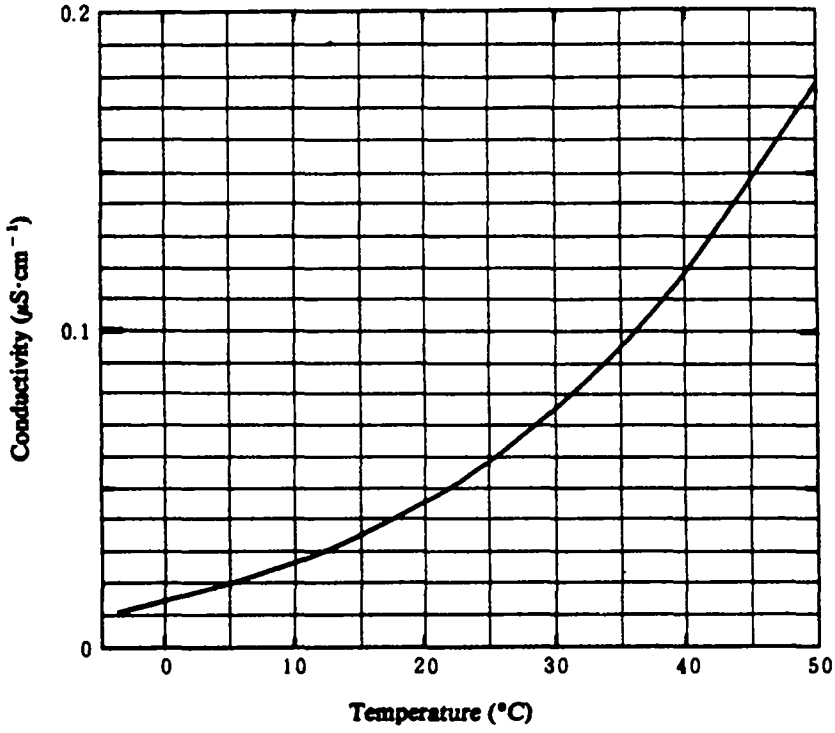

Fig. 1. Temperature–conductivity characteristics of deionized water (10 μseimens maximum).

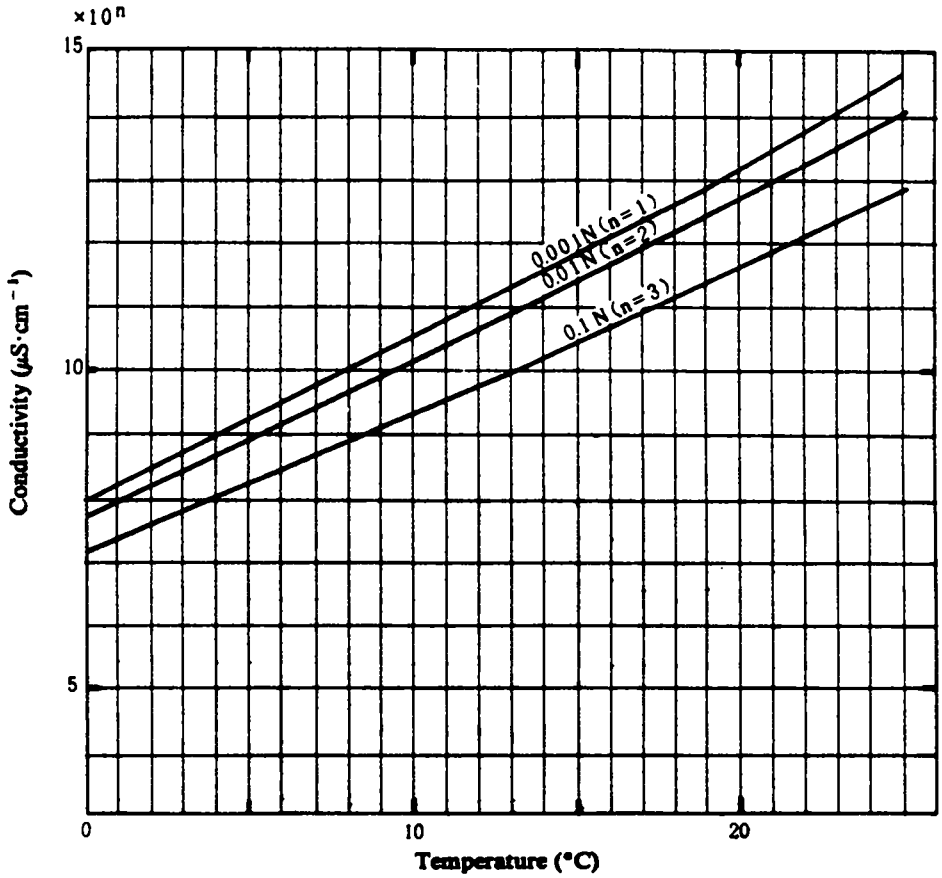

Fig. 2. Temperature–conductivity characteristics of standard potassium chloride solution.

TCLP ELEMENTS FOR WATER AND SOIL — QC SAMPLE PREPARATION

Analyte: Ba, Cd, Cr, Pb, As, Se, Ag	**Method No.:** QCI110
Matrix: Water, soil	**Spike Range:** 0.010-30 mg/L, dependent on the analyte and analytical method (see Step 1.5)
Procedure: TCLP followed by ICPAES, FAA, or ETVAA	**Accuracy and Precision:** 100% ± 4.2% RSD for all metals
Effective Date: 07/07/89 to 11/18/93	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water is spiked with standard solutions of the metals extracted by the Toxicity Characteristic Leaching Procedure (TCLP).

1.2. The acidified water QC sample represents the solution resulting from the extraction of TCLP metals from a soil matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure or those sections of the procedure that are applicable.

1.4. The methods of analysis for seven TCLP metals include electrothermal vaporization atomic absorption (ETVAA) spectroscopy, flame atomic absorption (FAA) spectroscopy, and inductively coupled plasma atomic emission spectrometry (ICPAES).

1.5. The QC spike range depends on the metal of interest and on the method of analysis. Refer to the following table for spike ranges.

SPIKE RANGES FOR TCLP METALS			
Analyte	FAA (mg/L)	ETVAA (mg/L)	ICPAES (mg/L)
Ag	0.25-1.0	-	0.3-6
As	-	0.01-0.06	1.5-30
Ba	2.0-8.0	-	0.2-5
Cd	0.5-1.5	0.001-0.005	0.2-3
Cr	0.5-1.5	0.01-0.06	0.3-6
Pb	0.5-1.5	0.01-0.06	2-30
Se	-	0.01-0.06	2-30

1.6. Mercury is included as a TCLP metal but is prepared separately. The Hg standard solution must be stored in a glass container with $Cr_2O_7^{=}$ added to stabilize the Hg. Refer to QC procedure QCI200 for the preparation and storage of Hg QC samples.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the pipette and the volumetric flask. A relative standard deviation (RSD) of 4.2% at the 1σ level has been calculated for the error of the standard and for the spiking and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

OIL AND GREASE IN WATER — QC SAMPLE PREPARATION

Analyte: Oil and grease	**Method No.:** QCI120
Matrix: Water	**Spike Range:** 20–100 mg/L
Procedure: Gravimetry	**Accuracy and Precision:** 100% ± 0.8% RSD
Effective Date: 02/02/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Reagent water is spiked with vegetable oil to prepare a quality control (QC) sample for oil and grease in water.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the balance. Since the analyst takes the sample to dryness, it is not necessary to dilute the sample to exactly one liter, and the assumption is made that L = 1. A relative standard deviation (RSD) of 0.8% at the 1-σ level has been calculated for the weighing process based on the following function:

$$D = \frac{M1}{L} ,$$

where D = calculated result,
M1 = weighing error, and
L = 1.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . .(variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R^2_{M1} / L} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of balance, and
L = 1.

2.2. Analysis by gravimetry of QC samples prepared from 1990 through 1993 using this procedure gave the following recoveries. The data are published in Source Materials 10.1. through 10.3.

TABLE I. SPIKE RECOVERY DATA FOR OIL/GREASE IN WATER

	Mean ± std dev (%)	Number of Samples
1990	91 ± 8	13
1991	95 ± 4	8
1992	94 ± 12	14
1993	94 ± 8	11

3. Collection and Storage of Samples

3.1. QC samples are prepared in 1-L jars with Teflon-lined lids and are refrigerated pending analysis.

4. Apparatus

4.1. Glass jars: 1-L, with Teflon-lined screw-cap lids.

4.2. Weighing dish: small, polyethylene.

4.3. Sample dropper: glass or polyethylene.

4.4 Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.5. Labels printed with QC sample numbers.

5. Reagents

5.1. Freon. Used to transfer the oil into the water.

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Type I, II, and III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. Spike QC samples with a pure vegetable oil, such as one used in cooking.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include 3 mL of Freon in 1 L of reagent water in a jar with a Teflon-lined lid to be used as a blank.

7.2. Place a small polyethylene weighing dish on the balance. Tare the balance.

7.3. Using a sample dropper, add vegetable oil to the weighing dish to reach the desired spike range and record the weight.

7.4. Fill a 1-L glass jar nearly full of reagent water. The analyst will use the entire sample, assuming the volume to be 1 L.

7.5. Using a clean sample dropper and less than 3 mL of Freon, quantitatively transfer the oil from the weighing dish into the water in the 1-L jar.

7.6. Place the Teflon-lined lid on the jar and label it with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter the information into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of oil and grease in the water as mg/L.

8.2. Calculate the spike concentration as in the following example.

8.2.1. If 50 mg of vegetable oil is quantitatively transferred into 1 L of reagent water, the oil and grease concentration in the water is 50 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

9. Proper Waste Disposal Practices

9.1. The hazardous components of an oil and grease sample are organic compounds. Dispose of waste as waste contaminated with organic compounds.

9.2. Solid waste.

9.2.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.2.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.2.3. Open the can only for the period of time necessary to add waste to it.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.2.5. Place a new plastic bag into the waste can for continued use.

9.2.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.2.7. Send a reference to the current Waste Profile Form (WPF) describing the waste along with the sealed bag.

9.2.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.2.9. The larger container has a sealing cover. Open the can only for the period of time necessary to add waste to it.

9.2.10. When the plastic bag liner is full, seal it with tape and keep in the sealed container pending pickup by Waste Management (CST-7).

9.3. Liquid waste.

9.3.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, out-of-date stock solutions, excess QC samples, and incorrectly spiked samples) in a covered metal can in a secondary containment tray and keep segregated from PCB-contaminated liquid waste.

9.3.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.3.3. Open the can only for the period of time necessary to add waste to it.

9.3.4. When the can is full, cap it and keep it in the secondary containment trap pending pickup by CST-7.

9.3.5. Label a new can for further use.

9.4. Waste pickup.

9.4.1. Request CST-7 to pick up a full container or can of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request form. The current WPF that describes the waste is referenced on the Chemical Waste Disposal Request.

9.4.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. B. Brooks, W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and HEalth Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5 "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1179-72 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN BULK MATERIALS — QC SAMPLE PREPARATION

Analytes: Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Se, Tl, Zn	**Method No.:** QCI135
Matrix: Oil	**Spike Range:** 0.2–20 μg/g, dependent on the analytical method (see Table I)
Procedure: Analysis by ICPMS, ICPES, ETVAA, or CVAA	**Accuracy and Precision:** 100% ± 2.0% RSD
Effective Date: 02/08/93	**Authors:** Michael N. Jasperson Nancy Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.1 for proper waste disposal practices.

1. Principle of Method

1.1. Obtain or prepare single-element or multi-element standards in oil.

1.2. The concentration of the working standards should be approximately 100 μg/g.

1.2.1. As, Se, and Hg standards may be obtained as single-element standards because of their relative instability at low concentrations in oil.

1.3. Spike an aliquot of each standard into a vial to reach the desired spike range. Dilute as necessary with base oil.

1.3.1. As, Se, and Hg quality control (QC) samples may be prepared separately because of their relative instability at low concentrations in oil.

1.4. The methods of analysis are inductively coupled plasma–mass spectrometry (ICPMS), inductively coupled plasma–atomic emission spectroscopy (ICPES), electrothermal vaporization atomic absorption (ETVAA) spectroscopy, or cold vapor atomic absorption (CVAA) spectrometry.

1.5. The QC spike range depends on the analytical method. Refer to Table I for the spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN OIL				
Analtye	ICPMS µg/g	ICPES µg/g	ETVAA µg/g	CVAA µg/g
Ag	0.2 - 12.5	1.0 - 20.0		
As	0.2 - 12.5		0.2 - 12.5	
Ba	0.2 - 12.5	1.0 - 20.0		
Cd	0.2 - 12.5	1.0 - 20.0		
Cr	0.2 - 12.5	1.0 - 20.0		
Hg				1.0 - 5.0
Ni	0.2 - 12.5.	1.0 - 20.0		
Pb	0.2 - 12.5	1.0 - 20.0		
Se	0.2 - 12.5		0.2 - 12.5	
Tl	0.2 - 12.5	1.0 - 20.0		
Zn	0.2 - 12.5	1.0 - 20.0		

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the analytical balance and the volumetric flask. A relative standard deviation (RSD) of 2% at the 1-σ level has been calculated for the error of the standard and for the weighing and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error, see 6.2.1,
M3 = weighing error, see 6.2.6,
M4 = weighing error, see 7.3.1, and
M5 = weighing error, see 7.3.4.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate RSD deviation using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.3. All variables contributing to the error associated with the preparation of these QC samples were considered. The largest errors were used in the error propagation calculations.

2.2. Results of analysis by ICPMS, ICPES, ETVAA, and CVAA of QC samples prepared during 1993 using these procedures are summarized in Table II below.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN BULK MATERIAL

Analyte	1993 Mean ± std dev (%)	N[a]
Ag	104 ± 2	4
As	68 ± 34	3
Ba	103 ± 11	4
Cd	100 ± 3	4
Cr	104 ± 3	4
Hg	82 ± 2	4
Ni	99 ± 3	2
Pb	103 ± 6	4
Se	81 ± 30	4
Tl	18 ± 4	2
Zn	—	—

N[a] = number of samples

3. Collection and Storage of Samples

3.1. The QC samples are prepared as close as possible to the time of analysis because all elements are unstable at low concentrations.

4. Apparatus

4.1. Glass vials: 5-mL, with Teflon-lined lids.

4.2. Pasteur pipettes: polyethylene, disposable.

4.3. Bottles: 60-mL, high-density polyethylene.

4.4. Bottles: 60-mL, amber high-density polyethylene.

4.5. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Conostan 75 Base Oil or equivalent: Conostan, Inc., P.O. Box 1267, Ponca City, OK 74603.

5.2. Conostan stabilizer or equivalent: Conostan, Inc., P.O. Box 1267, Ponca City, OK 74603.

6. Calibration and Standards

6.1. Obtain single-element or multi-element standards in oil with a concentration of approximately 100 μg/g.

6.2. Alternatively, prepare 100-μg/g metals in oil standards from 5000-μg/g metals in oil standards.

6.2.1. Add 500 mg of a 5000-μg/g metals in oil standard to a clean, tared, 60-mL high-density polyethylene bottle.

6.2.2. Record the mass added. **DO NOT** tare the balance.

6.2.3. Repeat Step 6.2.1 for each of the remaining 5000-μg/g standards desired in the dilution.

6.2.4. Add 150–200 mg of commercial stabilizer solution to achieve 0.6–0.8% by weight of stabilizer after dilution.

6.2.5. Record the mass added. **DO NOT** tare the balance.

6.2.6. Add the manufacturer's 75 Base Oil to bring the total mass to 25.0 g.

6.2.7. Cap and mix the standard by inversion.

6.2.8. Label the bottle with information identifying the standard.

6.2.9. Prepare the silver standard in an amber polyethylene bottle or an uncolored polyethylene bottle completely wrapped in aluminum foil to protect the silver from photodegradation.

6.3. Check the concentration of the 100-μg/g As, Se, and Hg standards periodically. Discard and replace a standard when degradation is noted.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed as close to the time of analysis as possible because all of the metals are relatively unstable at the low concentrations made for QCs. Periodically omit one or more of the metal analytes from the QC sample as a blank for that metal.

7.2. Determine which analytical method will be used. Select the spike range for the method from Table I.

7.3. Preparation of QC samples containing all metals except mercury.

7.3.1. Add standards gravimetrically. Weigh an aliquot of a 100-μg/g single-element or multi-element standard into a 5-mL glass vial with Teflon-lined lid to reach the desired spike range determined from Table I.

7.3.2. Record the standard used and mass added. **DO NOT** tare the balance.

7.3.3. Repeat Steps 7.3.1 and 7.3.2 for each desired standard.

7.3.4. Add the manufacturer's 75 Base Oil to bring the total mass of the QC sample to 3 g.

7.3.5. Cap the vial and mix by inversion.

7.4. Preparation of a mercury QC sample.

7.4.1. Weigh an aliquot of the 100-μg/g Hg standard into a 5-mL glass vial with Teflon-lined lid to reach the desired spike range determined from Table I.

7.4.2. Record the mass added. **DO NOT** tare the balance.

7.4.3. Add 18–24 mg of commercial stabilizer solution to achieve 0.6–0.8% by weight of stabilizer after dilution.

7.4.4. Record the mass added. **DO NOT** tare the balance.

7.4.5. Add the manufacturer's 75 Base Oil to bring the total mass to 3 g.

7.4.6. Cap the vial and mix by inversion.

7.5. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of each metal in the QC sample as μg/g.

8.2. Calculate spike concentrations for each metal in the QC sample as in the following example.

8.2.1. If 0.2672 g of 100-μg/g As standard is diluted to 3.0027 g with 75 Base Oil, the concentration of As in the sample is 8.9 μg/g. Multiply the result by the RSD calculated in Step 2.1. to obtain the uncertainty.

$$\frac{(0.2672\ g)\ (100\ \mu g/g)}{3.0027\ g} = 8.9\ \mu g/g \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, and empty vials) that has been contaminated with organic compounds in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing trace metals in oil is accumulated in a polyethylene bottle in a secondary containment tray and kept segregated from any other accumulated waste.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace metal in oil waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up solid waste or a full bottle of liquid waste containing trace metals in oil by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

TRACE ELEMENTS ON FILTER MEDIA — QC SAMPLE PREPARATION

Analyte: Metals	**Method No.:** QCI140
Matrix: Filters	**Spike Range:** 0.01-4000 μg/filter, depending on analyte and analytical method
Procedure: ICPMS, ICPAES, ETVAA, or FAA	**Accuracy and Precision:** 100% ± 3.6% RSD
Effective Date: 01/01/84	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. One or more standard solutions of single metals are spiked onto filter papers, preferably of the same type used to collect the samples.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. The methods of analysis for these filters are inductively coupled plasma-mass spectrometry (ICPMS), inductively coupled plasma-atomic emission spectrometry (ICPAES), flame atomic absorption (FAA) spectroscopy, or electrothermal vaporization atomic absorption (ETVAA) spectroscopy.

1.4. The QC spike range depends on the metal of interest and the method of analysis. Refer to Table I for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS ON FILTER MEDIA

Analyte	FAA µg/filter	ETVAA µg/filter	ICPAES µg/filter	ICPMS µg/filter
Ag	2.5-10			0.2-1.0
Al	10-30		40-4000	
As		0.1-1.0	15-300	
Au				0.2-1.0
Ba			10-100	
Be	1-10		10-100	
Bi				0.05-0.5
Ca	10-30		100-500	
Cd		0.01-0.1	4-400	
Co			2-50	
Cr	5-20		10-100	
Cu	5-20		6-600	0.05-2
Fe	5-20		10-100	
Li	2-10		10-100	
Mn	5-20			
Mo			10-100	
Ni	5-20		10-100	0.2-1.0
Pb	5-20	0.2-1.0	10-100	0.05-0.2
Sb			20-300	
Se			20-300	
Sn		0.2-1.0		
Sr				1-5
Ta	5-15			1-5
Th				0.05-0.5
Tl		0.1-0.6	10-100	0.01-0.05
U				1-5
Zn			2-30	0.2-1.0

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the pipette. A relative standard deviation (RSD) of 3.6% at the 1-σ level has been calculated for the error of the standard and for the spiking process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = standard error, and
M2 = spiking error.

2.1.1. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2}} \times 100 \quad ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.1.3. If two pipettes ($P_1 + P_2$) are used to add the analyte to the filter paper, use the following equation to calculate the pipetting error:

$$R_{M2} = \frac{\sqrt{\sigma_1^2 + \sigma_2^2}}{P_1 + P_2} \quad ,$$

where σ_1 = standard deviation of first pipette,
σ_2 = standard deviation of second pipette,
P_1 = mean of first pipette, and
P_2 = mean of second pipette.

Square R_{M2} and substitute this value in the equation in Step 2.1.2 to calculate the percent RSD for the use of two pipettes.

2.2. Analytical results from QC samples prepared between 1990 and 1991 using this procedure and analyzed by ICPMS, ICPAES, ETVAA, and FAA are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN FILTERS

Element	1990 mean ± std dev (%)	N[a]	1991 mean ± std dev (%)	N[a]
Al	98 ± 0	(2)	—	—
As	—	—	97 ± 2	(3)
Ba	122 ± 29	(7)	101 ± 0	(2)
Be	99 ± 9	(200)	102 ± 10	(170)
Ca	118 ± 25	(6)	—	—
Cd	104 ± 8	(19)	98 ± 9	(18)
Cr	101 ± 24	(30)	101 ± 8	(15)
Cu	113 ± 26	(13)	95 ± 14	(6)
Fe	127 ± 73	(23)	99 ± 5	(12)
Li	—	—	100 ± 0	(2)
Mn	97 ± 6	(6)	89 ± 0	(2)
Mo	—	—	88 ± 27	(8)
Ni	106 ± 12	(14)	98 ± 7	(12)
Pb	102 ± 14	(138)	104 ± 24	(78)
Sn	25 ± 0	(2)	—	—
Ta	—	—	62 ± 38	(5)
Th	—	—	79 ± 21	(15)
Tl	96 ± 78	(60)	220 ±380	(22)
U	104 ± 11	(51)	98 ± 15	(20)

N[a] = number of samples

3. Collection and Storage of Samples

3.1. QC samples are dried after spiking and stored in cellophane envelopes at room temperature pending analysis.

4. Apparatus

4.1. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.2. Spatula.

4.3. Platinum crucibles: approximately 50-mL capacity, with platinum covers. Each crucible should have a unique identifying number stamped or etched into it.

4.4. Desiccator.

4.5. Beaker: 50- mL, glass.

4.6. Flasks: 100- and 500-mL, volumetric, class A, glass.

4.7. Pipette: 10- mL, volumetric, class A, glass.

4.8. Graduated cylinder: 25-mL.

4.9. Filter paper: usually 1¼-in.-diam, cellulose acetate or paper filters, such as Whatman No. 41 or 42.

4.10. Auto-pipette: 100-μL, Rainin or equivalent.

4.11. Pipette tips: disposable.

4.12. Microsyringes: 10- and 25-μL capacity, gas-tight.

4.13. Envelopes: cellophane.

4.14. Filter containers: plastic.

4.15. Filter support: clean polyethylene bottle caps or beakers or similar support, slightly smaller in diameter than the filters to be spiked.

4.16. Heat lamp.

5. Reagents

5.1. Hydrochloric acid (ultrapure, suitable for trace-metal analysis).

5.2. Nitric acid (ultrapure, suitable for trace-metal analysis).

5.3. Water (double-deionized, 18-MΩ/cm or greater resistivity, specified in document ASTM-D1193 as ASTM Type I water and referred to in this procedure as double-deionized water).

6. Calibration and Standards

6.1. Use spectroscopy-grade metal standards (100-10,000 μg/mL) such as those from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the type and concentration of acid in the dilution to those in the concentrated standard.

6.3. Solutions of the analyte of interest in the concentration range 100-10,000 μg/mL may be prepared from analytical-grade compounds for use as standards if suitable standard solutions are not readily available.

6.4. Prepare a standard for the determination of total uranium and $^{235}U/^{238}U$ isotopic ratios through ICPMS by dissolving a certified natural U_3O_8 standard, such as National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 950b, in 7.8 M HNO_3. The uranium concentration of the standard should be 1 mg/mL. The $^{235}U/^{238}U$ isotopic ratio of natural uranium is 0.0072.

6.4.1. Use ultrapure HNO_3 and double-deionized water to prepare the uranium standard solutions. Prepare 7.8 M HNO_3 by diluting 25 mL of concentrated HNO_3 to 50 mL with double-deionized water. Prepare 1.6 M HNO_3 by diluting 1 mL of concentrated HNO_3 to 10 mL with double-deionized water. Prepare 1% HNO_3 by diluting 5 mL of concentrated HNO_3 to 500 mL with double-deionized water.

6.4.2. Weigh 1 g of certified natural U_3O_8 into a platinum crucible. Cover the crucible with the platinum lid.

6.4.3. Heat the U_3O_8 in a muffle furnace at 900°C for 1 h.

6.4.4. Cool the U_3O_8 in a desiccator overnight.

6.4.5. Accurately weigh 590 ± 1 mg of the U_3O_8 into a 50-mL beaker.

6.4.6. With gentle heating, dissolve the U_3O_8 in 20 mL of 7.8 M ultrapure HNO_3.

6.4.7. Evaporate the solution to near dryness.

6.4.8. Redissolve the residue in 10 mL of 1.6 M HNO_3.

6.4.9. Quantitatively transfer the uranium solution into a 500-mL volumetric flask with 1% HNO_3 and dilute the solution to volume with 1% HNO_3.

6.4.10. Calculate the concentration of the resultant natural uranium standard as in the example in Step 8.1.

6.5. Make a uranium standard with a concentration of 100 μg/mL by diluting the 1 mg/mL uranium standard. Use double-deionized water and ultrapure HNO_3.

6.5.1. Place approximately 70 mL of double-deionized water into a 100-mL volumetric flask.

6.5.2. Add 1 mL of concentrated HNO_3 to the flask to achieve a final acid concentration of 1%.

6.5.3. Add 10 mL of the 1 mg/mL natural uranium standard to the volumetric flask using a volumetric pipette.

6.5.4. Dilute the solution to volume with double-deionized water.

6.5.5. Calculate the concentration of the resultant natural uranium standard. The $^{235}U/^{238}U$ isotopic ratio in the standard is 0.0072.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include a nonspiked filter to be used as a blank.

7.2. Select a standard solution containing the analyte of interest in a concentration such that a minimum amount of the standard will be needed to reach the desired spike range.

7.3. An auto-pipette may be used for spike volumes within the acceptable range of the auto-pipette. Microsyringes should be used for smaller spike volumes.

7.4. The volume of standard solution added to the filter at one time should never be large enough to allow contact of the solution with the filter support, which could cause loss of solution to the support. To add larger volumes of standard, it may be necessary to add the standard in more than one aliquot, allowing the filter to dry after each addition.

7.5. Place a filter paper on a bottle cap or beaker or similar so such that most of the filter is within the rim of the support.

7.6. Spike the standard solution onto the filter to reach the desired spike range.

7.7. If more than one analyte will be spiked on the filter, dry the filter after addition of each standard solution.

7.8. Dry the filters under a heat lamp or allow them to air dry.

7.9. Place the dried filters in cellophane envelopes, segregating the different analyte combinations and concentrations.

7.10. Label each envelope with a QC sample number.

7.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter the information into the CVS and CVD databases on the VAX.

7.12. National Institute for Occupational Safety and Health (NIOSH) Proficiency Analytical Testing (PAT) intercomparison samples.

7.12.1. Prepare filters using the metals designated by NIOSH as being included in the current set of intercomparison samples. Follow Steps 7.5 through 7.11 above. Refer to Table III for spike ranges.

TABLE III. SPIKE RANGES FOR NIOSH PAT FILTERS

Cr	5-100 μg/filter
Pb	15-100 μg/filter
Cd	5-25 μg/filter
Zn	50-200 μg/filter

7.12.2. Obtain a NIOSH-PAT filter sample from a previous intercomparison round and assign it a QC sample number as an additional QC sample.

7.12.3. Record the sample identification, concentration, and uncertainty supplied by NIOSH for the filter in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.12.4. Place the four QC samples into plastic filter containers or clean cellophane envelopes, label with QC sample numbers, and distribute with the NIOSH-PAT intercomparison samples.

8. Calculations

8.1. Calculate the concentration of the uranium standard solution using the following atomic weights and example.

8.1.1. The atomic weight of U is 238.029, and the atomic weight of O is 16. The molecular weight of U_3O_8 recorded on the bottle label for the NIST SRM U_3O_8 may also be used.

8.1.2. The purity of the NIST U_3O_8 is recorded on the certificate for the SRM used.

8.1.3. If 589.6 mg of 99.968% pure U_3O_8 that has been heated in the muffle furnace is dissolved in acid and diluted to 500 mL, the uranium concentration in the standard will be 1.0 g/L.

$$\frac{\left(\frac{714.087 \text{ g U}}{842.0822 \text{ g } U_3O_8}\right)(0.99968)\ (0.5896 \text{ g})}{(500 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 1.0 \text{ g/L}$$

8.1.4. The $^{235}U/^{238}U$ isotopic ratio in natural uranium is 0.0072 ± 0.0007.

8.2. Record sample concentrations as mg/filter, μg/filter, or ng/filter.

8.3. Calculate the spike concentration for each metal in the QC sample as in the following example.

8.3.1. If 30 μL of a 100-μg/mL beryllium standard is spiked onto a cellulose acetate filter, the concentration of Be in the QC sample is 3 μg/filter. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(100 \text{ μg/mL})\ (1 \text{ mL}/1000 \text{ μL})\ (30 \text{ μL})}{\text{filter}} = 3 \text{ μg/filter}$$

9. Proper Waste Disposal Practices

9.1. Solid Waste

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form describing the solid waste is completed and sent to Waste Management (CST-7) for review.

9.1.2.2. If the CST-7 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If the CST-7 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid Waste

9.2.1. Liquid waste containing hazardous contaminants, such as solutions of trace metals, is accumulated in a coated glass bottle in a secondary containment tray and kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by the CST-7.

9.2.5. A new bottle is labeled for further use.

9.3. Waste Pickup

9.3.1. Request CST-7 to pickup solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request form (CWDR). The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, E. A. Jones, N. L. Koski, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 950b, Uranium Oxide (U_3O_8)" (National Institute of Standards and Technology, Washington, DC, March 1978).

10.4. "Hazardous, and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN SOLVENT — QC SAMPLE PREPARATION

Analytes: Ag, As, Ba, Cd, Cr, Hg, Ni, Pb, Se, Tl, Zn	**Method:** QCI150
Matrix: Kerosene, xylenes, methyl isobutyl ketone, and d-limonene	**Spike Range:** 300-1300 μg/L, dependent on the analytical method (see Table I)
Procedure: Analysis by ICPMS, FAA, ETVAA, or CVAA	**Accuracy and Precision:** 100% ± 5.1% RSD
Effective Date: 04/01/87 to 01/01/94	**Authors:** Nancy Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the EM-9 Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Obtain or prepare trace elements in oil standards.

1.2. Prepare working standards in base oil at approximately 100 μg/g for Ag, As, Ba, Cd, Cr, Ni, Pb, Se, Tl, and Zn, and 5 μg/g for Hg.

1.3. Spike an aliquot of each element into a polypropylene centrifuge tube. The analyst will dilute the sample to volume with the desired solvent before analysis.

1.4. The methods of analysis are inductively coupled plasma mass spectrometry (ICPMS), flame atomic absorption (FAA) spectroscopy, electrothermal vaporization atomic absorption (ETVAA) spectroscopy, or cold vapor atomic absorption (CVAA) spectrometry.

1.5. The QC spike range depends on the analytical method. Refer to Table I for the spike ranges.

TABLE I. SPIKE RANGES FOR METALS IN SOLVENT			
Element	Method	Spike range (μg/L)	Typical solvent
Ag, As, Ba, Cd, Cr, Ni, Pb, Se, Tl, Zn	ICPMS	300-800	kerosene or xylenes
Ag, As, Ba, Cd, Cr, Ni, Pb, Se, Tl, Zn	ETVAA	300-800	methyl isobutyl ketone or xylenes
Ag, As, Ba, Cd, Cr, Ni, Pb, Se, Tl, Zn	FAA	700-1300	d-limonene or xylenes
Hg	CVAA	2-4	1% nitric acid

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the analytical balance and the volumetric flask. A relative standard deviation (RSD) of 5.1% at the 1σ level has been calculated for the error of the standard and for the weighing and dilution process based on the following function:

$$D = \frac{M_1 \times M_2}{M_3} ,$$

where D = calculated result,
M_1 = standard error,
M_2 = weighing error, and
M_3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

TRACE ELEMENTS IN NITRIC ACID — QC SAMPLE PREPARATION

Analyte: Metals	**Method No.:** QCI170
Matrix: Water, soil	**Accuracy and Precision:** 100% ± 4.3% RSD
Procedure: ICPMS, ICPAES, FAA, ETVAA, or CVAA, depending on metal and concentration range	**Spike Range:** 1 μg/L-200 mg/L
Effective Date: 04/01/88	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water is spiked with standard solutions of metals.

1.2. An acidified water quality control (QC) sample represents the solution resulting from the extraction of the metals from a soil matrix and is analyzed from that point using the same analytical procedure applied to the unknown samples.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed using the same analytical procedure or applicable sections of the procedure.

1.4. Methods of analysis depend on the metal and its concentration. They include inductively coupled plasma-mass spectrometry (ICPMS), inductively coupled plasma-atomic emission spectrometry (ICPAES), flame atomic absorption (FAA) spectroscopy, electrothermal vaporization atomic absorption (ETVAA) spectroscopy, and cold vapor atomic absorption (CVAA) spectroscopy.

1.5. The QC spike range depends on the metal of interest and the method of analysis. Refer to Table I below for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN NITRIC ACID

Analyte	ETVAA/ICPMS mg/L	FAA/ICPAES mg/L	CVAA mg/L
Al	0.05-0.2	1-200	
Ag	0.01-0.10	0.2-2.0	
As	0.01-0.10	0.1-5.0	
B	0.02-0.20	0.5-30	
Ba	0.01-0.10	0.1-10	
Be	0.01-0.10	0.05-2	
Ca		1-200	
Cd	0.01-0.10	0.1-5	
Co	0.01-0.10	0.1-5	
Cr	0.01-0.10	0.1-5	
Cu	0.01-0.10	0.1-5	
Fe	0.02-0.50	1.0-6	
Hg			0.001-0.010
K	0.02-0.50	1.0-20	
Li	0.01-0.10	0.1-5	
Mg	0.02-0.50	1.0-20	
Mn	0.01-0.10	0.1-5	
Mo	0.01-0.10	0.1-5	
Na	0.02-0.50	1.0-20	
Ni	0.01-0.10	0.1-5	
Pb	0.01-0.10	1.0-20	
Sb	0.01-0.10	0.2-5	
Se	0.005-0.10	0.2-5	
Sn	0.01-0.10	0.2-2	
Sr	0.01-0.10	0.1-5	
Ti	0.01-0.10	1.0-20	

TABLE 1. SPIKE RANGES FOR TRACE ELEMENTS IN NITRIC ACID (cont)			
Analyte	ETVAA/ICPMS mg/L	FAA/ICPAES mg/L	CVAA mg/L
Tl	0.01-0.10	5.0-20	
U	0.01-0.10		
V	0.02-0.10	0.2-20	
Zn	0.01-0.1	0.2-2	

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and the error associated with the use of the pipette and the volumetric flask. A relative standard deviation (RSD) of 4.3% at the 1-σ level has been calculated for the spiking and dilution process based on the following functions.

2.1.1. One dilution of the standard.

2.1.1.1. Use the following function for standards requiring a single dilution:

$$U = \frac{M_1 \times M_2}{M_3} ,$$

where U = uncertainty,
M_1 = standard error,
M_2 = spiking error, and
M_3 = dilution error.

2.1.1.2. Calculate relative variance for each variable using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where $R^2{}_M$ = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.1.3. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 \quad ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.2. Two dilutions of the standard.

2.1.2.1. Use the following function for standards requiring a second dilution:

$$U = \frac{M_1 \times M_2}{M_3} \times \frac{M_4}{M_5} \quad ,$$

where U = uncertainty of standard,
M_1 = standard error,
M_2 = first spiking error,
M_3 = first dilution error,
M_4 = second spiking error, and
M_5 = second dilution error.

2.1.2.2. Calculate relative variance for each variable using the following equation:

$$R^2_M = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2.3. Calculate RSD using the following equation:

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5}} \times 100 \quad ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of first pipette,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of second pipette,
R^2_{M5} = relative variance of second volumetric flask, and
100 = factor to convert to percentage.

2.2. All variables contributing to the error associated with the preparation of these QC samples were considered. The largest errors were used in the error propagation calculations.

2.3. Analytical results from QC samples prepared between 1990 and 1991 using this procedure and analyzed by ICPMS, ICPAES, FAA, ETVAA, or CVAA are summarized in Table II. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN NITRIC ACID

Analyte	1990 Mean ± std dev (%)	N[a]	1991 Mean ± std dev (%)	N[a]
Ag	99 ± 15	(65)	99 ± 9	(167)
Al	109 ± 26	(126)	104 ± 16	(42)
As	97 ± 18	(67)	102 ± 10	(119)
Au	84 ± 0	(1)	218 ± 0	(1)
B	98 ± 16	(77)	102 ± 5	(30)
Ba	105 ± 16	(73)	101 ± 12	(159)
Be	102 ± 18	(102)	96 ± 13	(82)
Ca	114 ± 16	(14)	113 ± 9	(14)
Cd	99 ± 8	(72)	102 ± 9	(171)

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN NITRIC ACID (cont)

Analyte	1990 Mean ± std dev (%)	N[a]	1991 Mean ± std dev (%)	N[a]
Ce	—	—	—	—
Co	109 ± 37	(39)	106 ± 8	(37)
Cr	104 ± 13	(60)	102 ± 7	(179)
Cu	107 ± 36	(95)	101 ± 7	(82)
Fe	101 ± 40	(40)	103 ± 7	(54)
Hg	99 ± 13	(167)	98 ± 12	(83)
K	99 ± 7	(13)	102 ± 7	(14)
Li	99 ± 11	(10)	130 ± 8	(5)
Mg	103 ± 6	(31)	105 ± 7	(19)
Mn	106 ± 29	(60)	104 ± 22	(37)
Mo	101 ± 18	(61)	103 ± 10	(34)
Na	107 ± 10	(21)	109 ± 15	(23)
Ni	104 ± 26	(128)	101 ± 10	(88)
Pb	105 ± 32	(70)	102 ± 7	(199)
Re	—	—	—	—
S	115 ± 13	(15)	113 ± 14	(16)
Sb	101 ± 16	(111)	98 ± 10	(49)
Sc	—	—	—	—
Se	100 ± 8	(74)	100 ± 10	(134)
Si	100 ± 4	(71)	100 ± 4	(48)
Sr	98 ± 5	(61)	100 ± 9	(12)
Ta	—	—	—	—
Th	—	—	104 ± 9	(21)
Tl	105 ± 23	(100)	102 ± 9	(59)
U	98 ± 11	(262)	100 ± 11	(160)
U-235/238	100 ± 6	(119)	100 ± 5	(85)
V	102 ± 20	(40)	103 ± 11	(25)
Y	-	—	—	
Zn	104 ± 39	(79)	103 ± 11	(57)

N[a] = number of samples.

3. Collection and Storage of Samples

3.1. Mercury standard samples must be stored in glass containers with $Cr_2O_7^=$ added as a stabilizer. Refer to Method No. QCI200 for the preparation and storage of Hg standard samples.

3.2. If the QC sample contains Ag, it must be protected from light to prevent reduction and subsequent loss of Ag. Store the sample at room temperature in an amber high-density polyethylene bottle or in an uncolored high-density polyethylene bottle completely wrapped in aluminum foil.

3.3. If any of the metal standard solutions contains HCl, it may not be added to a solution containing Ag because the Ag will be lost as insoluble AgCl.

3.4. QC samples are prepared in a volumetric flask and are aliquoted into high-density polyethylene bottles for storage at room temperature pending analysis.

4. Apparatus

4.1. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.2. Spatula.

4.3. Platinum crucible: approximately 50-mL capacity, with platinum cover. The crucible should have a unique identifying number stamped or etched into it.

4.4. Desiccator.

4.5. Beaker: 50-mL, glass.

4.6. Volumetric flasks: 10-, 50-, 100-, and 500-mL, class A, glass.

4.7. Graduated cylinders: 10- and 25-mL.

4.8. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.9. Pipette tips: disposable.

4.10. Volumetric pipettes: 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 10-mL, class A, glass.

4.11 Bottles: 125- and 250-mL, high-density polyethylene.

4.12. Aluminum foil.

4.13. Bottles: 125- and 250-mL, amber, high-density polyethylene.

4.14. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (16 M, ultrapure, suitable for trace-metal analysis).

5.2. Water (double-deionized, 18-MΩ/cm or greater resistivity, specified in document ASTM-D1193 as ASTM Type I water and referred to in this procedure as double-deionized water).

5.3. Potassium dichromate (reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade metal standards (100-10,000 μg/mL) from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, or equivalent.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the kind and concentration of acid in the dilution to those in the concentrated standard.

6.3. Prepare a standard for the determination of Cr in the +6 oxidation state by dissolving reagent-grade $K_2Cr_2O_7$ in double-deionized water. The Cr^{+6} concentration of the standard should be 1000 μg/mL.

6.3.1. Tare a 50-mL volumetric flask on the balance.

6.3.2. Accurately weigh 141.5 ± 0.2 mg of analytical-grade $K_2Cr_2O_7$ into the flask.

6.3.3. Dissolve the salt and dilute the standard to volume with double-deionized water.

6.3.4. Calculate the Cr^{+6} concentration of the standard as in the example in Step 8.1.

6.4. Prepare a standard for the determination of total uranium and $^{235}U/^{238}U$ isotopic ratios through ICPMS by dissolving a certified natural U_3O_8 standard, such as National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 950b, in 7.8 M HNO_3. The uranium concentration of the standard should be 1 mg/mL. The $^{235}U/^{238}U$ isotopic ratio of natural uranium is 0.0072.

6.4.1. Use ultrapure HNO_3 and double-deionized water to prepare the uranium standard solutions. Prepare 7.8 M HNO_3 by diluting 25 mL of concentrated HNO_3 to 50 mL with double-deionized water. Prepare 1.6 M HNO_3 by diluting 1 mL of concentrated HNO_3 to 10 mL with double-deionized water. Prepare 1% HNO_3 by diluting 5 mL of concentrated HNO_3 to 500 mL with double-deionized water.

6.4.2. Weigh 1 g of a certified natural U_3O_8 into a platinum crucible. Cover the crucible with the platinum lid.

6.4.3. Heat the U_3O_8 in a muffle furnace at 900°C for 1 h.

6.4.4. Cool the U_3O_8 in a desiccator overnight.

6.4.5. Accurately weigh 590 ± 1 mg of the U_3O_8 into a 50-mL beaker.

6.4.6. With gentle heating, dissolve the U_3O_8 in 20 mL of 7.8 M ultrapure HNO_3.

6.4.7. Evaporate the solution to near dryness.

6.4.8. Redissolve the residue in 10 mL of 1.6 M HNO_3.

6.4.9. Quantitatively transfer the uranium solution into a 500-mL volumetric flask with 1% HNO_3 and dilute the solution to volume with 1% HNO_3.

6.4.10. Calculate the concentration of the resultant natural uranium standard as in the example in Step 8.2.

6.5. Prepare a uranium standard with a concentration of 100 μg/mL by diluting the 1-mg/mL uranium standard. Use double-deionized water and ultrapure HNO_3.

6.5.1. Place approximately 70 mL of double-deionized water into a 100-mL volumetric flask.

6.5.2. Add 1 mL of concentrated HNO_3 to the flask to achieve a final acid concentration of 1%.

6.5.3. Add 10 mL of the 1-mg/mL natural uranium standard to the volumetric flask using a volumetric pipette.

6.5.4. Dilute the solution to volume with double-deionized water.

6.5.5. Calculate the concentration of the resultant natural uranium standard. The $^{235}U/^{238}U$ isotopic ratio in the standard is 0.0072.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically omit one or more metals from the acidified standard as a blank QC for those metals.

7.2. This procedure describes the preparation of five 100-mL aliquots of multielement standard, five 100-mL aliquots of silver standard, and two 250-mL aliquots of natural uranium standard. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size as necessary.

7.3. For a multielement QC sample, a 100-mL minimum volume is needed for analysis by ICPMS or ETVAA, and a 200-mL minimum volume is needed for analysis by ICPAES or FAA.

7.3.1. Place approximately 400 mL of double-deionized water in a 500-mL volumetric flask.

7.3.2. Add 15 mL of 16 M ultrapure nitric acid to the water to produce a final acid concentration of 3% by volume.

7.3.3. Use a new disposable pipette tip to spike each metal standard solution into the QC sample to avoid contamination of the standards. Spike an aliquot of each metal standard solution into the acidified water in the flask to reach the desired spike range for that metal.

NOTE: If any of the metal standard solutions used to prepare the QC sample contains HCl, do not include Ag in the sample because it will be lost as insoluble AgCl. Prepare a separate QC sample for Ag.

7.3.4. Dilute the QC sample to volume with double-deionized water. Mix by inversion.

7.3.5. Divide the QC sample evenly among five 125-mL high-density polyethylene bottles. If Ag has been included in the sample, use amber 125-mL high-density polyethylene bottles or uncolored bottles completely wrapped in aluminum foil.

7.3.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.4. Preparing a separate Ag QC sample.

7.4.1. Place approximately 400 mL of double-deionized water into a 500-mL volumetric flask.

7.4.2. Add 15 mL of 16 M ultrapure nitric acid to produce a final acid concentration of 3% by volume.

7.4.3. Spike an aliquot of Ag standard solution into the acidified water in the flask to reach the desired spike range.

7.4.4. Dilute the QC sample to volume with double-deionized water. Mix by inversion.

7.4.5. Divide the QC sample evenly between five amber 125-mL high-density polyethylene bottles or five uncolored 125-mL high-density

polyethylene bottles. The uncolored bottles must be completely wrapped in aluminum foil to prevent loss of Ag.

7.4.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.5. For the determination of total uranium and $^{235}U/^{238}U$ isotopic ratios through ICPMS, prepare a QC sample from the natural uranium standard made from a certified natural U_3O_8 material.

7.5.1. Place approximately 400 mL of double-deionized water into a 500-mL volumetric flask.

7.5.2. Add 15 mL of ultrapure nitric acid to produce a final acid concentration of 3% by volume.

7.5.3. Spike an aliquot of 100-μg/mL natural uranium standard into the acidified water in the flask to reach the desired spike range for total uranium.

7.5.4. Dilute the QC sample to volume with double-deionized water. Mix by inversion.

7.5.5. Divide the QC sample evenly between two 250-mL high-density polyethylene bottles.

7.5.6. Label each bottle with a QC number and store at room temperature pending analysis. The same QC number may be used for both aliquots of a QC sample from the same 500-mL volumetric flask.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, isotopic ratio, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of the Cr^{+6} standard solution using the following atomic weights and example.

8.1.1. Atomic weight of K = 39.1
Atomic weight of Cr = 52.0
Atomic weight of O = 16.0

8.1.2. If 141.5 mg of $K_2Cr_2O_7$ is dissolved in 50 mL of double-deionized water, the Cr^{+6} concentration in the standard is 1000 μg/mL.

$$\frac{\left(\frac{104\ g\ Cr^{+6}}{294.2\ g\ K_2Cr_2O_7}\right)(141.5\ mg\ K_2Cr_2O_7)\left(\frac{1000\ \mu g}{1\ mg}\right)}{50\ mL} = 1000\ \mu g\ \frac{Cr^{+6}}{mL}$$

8.2. Calculate the concentration of the uranium standard solution using the following atomic weights and example.

8.2.1. Atomic weight of U = 238.029
Atomic weight of O = 16
The molecular weight of U_3O_8 recorded on the bottle label for NIST SRM U_3O_8 may also be used.

8.2.2. The purity of the NIST U_8O_8 is recorded on the certificate for the SRM used.

8.2.3. If 589.6 mg of 99.968% pure U_3O_8, which has been heated in the muffle furnace, is dissolved in acid and diluted to 500 mL, the uranium concentration in the standard will be 1.0 g/L.

$$\frac{\left(\frac{714.087\ g\ U}{842.0822\ g\ U_3O_8}\right)(0.99968)\ (0.5896\ g)}{(500\ mL)\ (1\ L/1000\ mL)} = 1.0\ g/L$$

8.2.4. The $^{235}U/^{238}U$ isotopic ratio in natural uranium is 0.0072 ± 0.0007.

8.3. Record the concentration of each metal in the QC sample as μg/L or mg/L.

8.4. Calculate spike concentrations for each metal in the QC sample as in the following example:

8.4.1. If 250 μL of a 100-μg/mL Se standard is used to spike 400 mL of acidified water and the solution is diluted to 500 mL, the concentration of Se in the sample is 50 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(100\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(250\ \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 50\ \mu g/L$$

8.4.2. If 450 μL of 1000-μg/mL Ag standard is used to spike 400 mL of acidified water and the solution is diluted to 500 mL, the concentration of Ag in the sample is 900 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(450\ \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 900\ \mu g/L$$

8.4.3. If 400 μL of 100-μg/mL natural uranium standard is used to spike 400 mL of acidified water and the solution is diluted to 500 mL, the concentration of U in the sample is 80 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(100\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(400 \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 80\ \mu g/L$$

8.4.4 The $^{235}U/^{238}U$ isotopic ratio in natural uranium is 0.0072 ± 0.0007.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form describing the solid waste is completed and sent to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants, such as solutions of trace metals, is accumulated in a coated glass bottle in a secondary containment tray and is kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-7.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request form (CWDR). The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, E. A. Jones, N. L. Koski, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 950b, Uranium Oxide (U_3O_8)" (National Institute of Standards and Technology, Washington, DC, March 1978).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN HYDROCHLORIC ACID — QC SAMPLE PREPARATION

Analyte: Metals	**Method No.:** QCI180
Matrix: Water, soil	**Spike Range:** Dependent on element and analytical method (see Step 1.5)
Procedure: ICPAES, FAA, or ETVAA, depending on metal and concentration range	**Accuracy and Precision:** 100% ± 5% RSD
Effective Date: 01/17/91	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water is spiked with standard solutions of metals. Tin and titanium are more stable in hydrochloric acid than in nitric acid.

1.2. The acidified water quality control (QC) sample represents the solution resulting from the extraction of the metals from a soil matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed from the extraction step in the same analytical procedure used for unknown samples.

1.4. The method of analysis depends on the metal and its concentration. The methods include inductively coupled plasma—atomic emission spectrometry (ICPAES), flame atomic absorption (FAA) spectroscopy, and electrothermal vaporization atomic absorption (ETVAA) spectroscopy. QC samples of trace elements in hydrochloric acid are not run by inductively coupled plasma—mass spectrometry (ICPMS) because the hydrochloric acid interferes.

1.5. The QC spike range depends on the metal of interest and on the method of analysis. Refer to Table I below for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN HYDROCHLORIC ACID			
Element	ICPAES (mg/L)	FAA (mg/L)	ETVAA (mg/L)
Sn	2-30	0.1-1	0.010-0.060
Ti	0.1-2	2-5	0.005-0.050

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 5.0% at the 1-σ level has been calculated for standard preparation and for the spiking and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where $R^2{}_M$ = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 \quad ,$$

where S_{D_T} = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.3. All variables contributing to the error associated with the preparation of these QC samples were considered. The largest errors were used in the error propagation calculations.

2.2. Analytical results from QC samples prepared between 1990 and 1991 using this procedure and analyzed by ICPAES, FAA, and ETVAA are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN HCL

Analyte	1990 Mean ± std dev (%)	N[a]	1991 Mean ± std dev (%)	N[a]
Sn	104 ± 7	(8)	91 ± 11	(13)
Ti	109 ± 34	(45)	105 ± 17	(22)

N[a] = number of samples.

3. Collection and Storage of Samples

3.1. QC samples are prepared in a volumetric flask and are aliquoted into high-density polyethylene bottles for storage at room temperature pending analysis.

4. Apparatus

4.1. Flasks: 200-mL, glass, class A volumetric.

4.2. Graduated cylinder: 100-mL.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Pipettes: 2-, 3-, 4-, 5-, and 6-mL, glass, class A volumetric.

4.6. Bottles: 125-mL, high-density polyethylene.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Hydrochloric acid (12 M, ultrapure, suitable for trace-metal analysis).

5.2. Water (double-deionized, >18-MΩ/cm resistivity, specified in document ASTM-D1193 as ASTM Type I water and referred to in this procedure as double-deionized water).

6. Calibration and Standards

6.1. Spectroscopy-grade metal standards (100-10,000 μg/mL) from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, or equivalent.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the type and concentration of acid in the dilution to those in the concentrated standard.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically omit one or more metals from the acidified sample as a blank QC for those metals.

7.2. This procedure describes the preparation of two 100-mL aliquots of a QC sample. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size and reagent volume as necessary.

7.3. Place approximately 100 mL of double-deionized water into a 200-mL volumetric flask.

7.4. Add 40 mL of ultrapure hydrochloric acid to the water in the flask.

7.5. Use a new disposable pipette tip to spike each metal standard solution into the QC sample to avoid contamination of the standards. Spike an aliquot of each metal standard solution into the acidified water in the flask to reach the desired spike range for that metal.

7.6. Dilute the QC sample to volume with double-deionized water. Mix by inversion.

7.7. Divide the QC sample evenly between two 125-mL high-density polyethylene bottles.

7.8. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for both aliquots of a QC sample from the same 200-mL volumetric flask.

8. Calculations

8.1. Record the concentration of each metal in the QC sample as μg/L or mg/L.

8.2. Calculate the spike concentration for each metal in the QC sample as in the following example.

8.2.1. If 3.0 mL of a 1000-μg/mL Sn standard is used to spike 180 mL of acidified water and the solution is diluted to 200 mL, the concentration of Sn in the sample is 15 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu g/mL)\ (3.0\ mL)\ (1\ mg/1000\mu g)}{(200\ mL)\ (1\ L/1000\ mL)} = 15\ mg/L$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form describing the solid waste is completed and sent to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants, such as solutions of trace metals, is accumulated in a coated glass bottle in a secondary containment tray and kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-7.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request form (CWDR). The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, E. A. Jones, N. L. Koski, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4 "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91, (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN WATER — QC SAMPLE PREPARATION

Analytes: Boron, bromide, calcium, chloride, fluoride, lithium, magnesium, phosphorus, potassium, silicon, sodium, sulfate	**Method No.:** QCI190
Matrix: Water	**Spike Range:** Dependent on the element (see Table I)
Procedure: FIA, ACOLOR, ISE, or IC	**Accuracy and Precision:** 100% ± 3% RSD
Effective Date: 10/01/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare individual standard solutions of bromide, chloride, fluoride, and sulfate salts in reagent water.

1.2. Obtain commercially prepared single-element solutions of boron, calcium, lithium, magnesium, phosphorus, potassium, silicon, and sodium.

1.3. Spike the chosen volume of each standard separately or in various combinations into reagent water or distilled water as specified in Sec. 7.

1.4. Methods of analysis depend on the analyte and its concentration. They include flow injection analysis (FIA), ion-selective electrode (ISE), ion chromatography (IC), and colorimetry (ACOLOR).

1.5. The quality control (QC) spike range depends on the analyte of interest and the analytical method. Refer to Table I for spike ranges.

TABLE I. SPIKE RANGES FOR TRACE ELEMENTS IN WATER

Analyte	Spike range (mg/L)	Analysis method
Chloride (Cl)	5.0-50	FIA/IC
Bromide (Br)	5.0-50	FIA/IC
Fluoride (F)	0.1-2.0	ISE
Sulfate (SO_4)	5.0-30	FIA/IC
Phosphorus (P)	0.04-1.0	ACOLOR
Boron (B)	0.1-6.0	FIA
Silicon (Si)	3-50	FIA
Silica (SiO_2)	5-100	FIA
Sodium (Na)	5-30	IC
Potassium (K)	3-20	IC
Calcium (Ca)	5-30	IC
Magnesium (Mg)	3-20	IC
Lithium (Li)	1-10	IC

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with the use of the pipette and volumetric flask. A relative standard deviation (RSD) of 3% at the 1-σ level has been calculated for the error of the standard and for the spiking and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percent.

2.1.3. If a second pipette is used to obtain the desired analyte concentration, use the following equation:

$$R_{M2} = \frac{\sqrt{\sigma_1^2 + \sigma_2^2}}{P_1 + P_2} ,$$

where σ_1 = standard deviation of first pipette error,
σ_2 = standard deviation of second pipette error,
P_1 = mean of first pipette, and
P_2 = mean of second pipette.

Square R_{M2} and substitute this value in the equation in Step 2.1.2 to calculate the percent RSD for the use of two pipettes.

2.2. Analytical results from QC samples prepared between 1990 and 1991 using this procedure and analyzed by FIA, ISE, ACOLOR, and IC are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SPIKE RECOVERY DATA FOR TRACE ELEMENTS IN WATER

Analyte	1990 mean ± std dev (%)	N[a]	1991 mean ± std dev (%)	N[a]
Na	107 ± 10	(21)	109 ± 15	(23)
SO_4	115 ± 13	(15)	113 ± 14	(16)
Si	100 ± 3	(4)	103 ± 0	(1)
K	99 ± 7	(13)	102 ± 7	(14)
P	120 ± 120	(9)	120 ± 60	(14)
Mg	103 ± 6	(31)	105 ± 7	(19)
Li	99 ± 11	(10)	130 ± 8	(5)
F	105 ± 10	(20)	113 ± 16	(13)
Cl	116 ± 19	(18)	119 ± 23	(13)
Ca	114 ± 16	(14)	113 ± 9	(14)
Br	120 ± 34	(10)	100 ± 12	(4)
B	98 ± 16	(77)	102 ± 5	(30)

N[a] = number of samples.

3. Collection and Storage of Samples

3.1. QC samples for boron, fluoride, and silicon are prepared in polypropylene flasks to avoid interactions with borosilicate glass. All other samples may be made in glass flasks.

3.2. Spiked QC samples are aliquoted and stored in high-density polyethylene bottles at room temperature pending analysis.

4. Apparatus

4.1. Flasks: 50-, 250-, and 500-mL, class A volumetric, glass.

4.2. Flasks: 50-, 100-, and 500-mL, volumetric, polypropylene, Nalgene or equivalent.

4.3. Spatula.

4.4. Pipettes: 1- and 2-mL, class A volumetric, glass.

4.5. Auto-pipette: 100-μL and 1000-μL, Rainin or equivalent.

4.6. Pipette tips: disposable.

4.7. Bottles: 60-, 125-, and 250-mL, high-density polyethylene.

4.8. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.9. Labels printed with QC sample numbers.

5. Reagents

5.1. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to ASTM Type I, II, or III and free of interferences with the analytical method.

5.2. Distilled water. Used to dilute silicon QC samples. Deionized water is not used because deionization may result in high levels of silicon when the resin begins to degrade, even though the resistivity of the water remains acceptable.

5.3. Potassium bromide (anhydrous, reagent-grade).

5.4. Sodium chloride (reagent-grade).

5.5. Sodium fluoride (reagent-grade).

5.6. Sodium sulfate (anhydrous, reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade metal standards (1000-10,000 μg/mL) from Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, or equivalent.

6.2. If a more dilute standard is needed to reach the desired spike range, dilute a concentrated standard, taking care to match the kind and concentration of acid in the dilution to those in the concentrated standard. Use distilled water to make dilutions of a silicon standard.

6.3. Standard solutions for bromide, chloride, fluoride, and sulfate are made from salts.

6.4. Thoroughly rinse all glassware before preparing standards. The presence of nitric acid may oxidize bromide ion to bromine; it will also interfere with analysis by IC by giving a broad nitrate ion peak, which may obscure the differentiation and quantitation of other anions present.

6.5. Prepare a standard solution of bromide ion at approximately 20 mg/mL using solid anhydrous potassium bromide.

6.5.1. Accurately weigh 1.5 ± 0.03 g of solid anhydrous potassium bromide into a 50-mL volumetric flask.

6.5.2. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.5.3. Dilute the solution to volume with reagent water and mix by inversion.

6.5.4. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.5.5. Record information on standard preparation in the QC Laboratory notebook.

6.6. Prepare a standard solution of chloride ion at approximately 20 mg/mL using sodium chloride.

6.6.1. Dry 2 ± 0.1 g of solid sodium chloride at approximately 140°C for 30 min before using it to prepare the standard chloride solution.

6.6.2. Accurately weigh 1.65 ± 0.04 g of dried sodium chloride into a 50-mL volumetric flask.

6.6.3. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.6.4. Dilute the solution to volume with reagent water and mix by inversion.

6.6.5. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.6.6. Record information on standard preparation in the QC Laboratory notebook.

6.7. Prepare a standard solution of fluoride ion at approximately 1000 μg/mL using solid sodium fluoride.

6.7.1. Make the fluoride standard in a polypropylene (Nalgene) volumetric flask to avoid reaction of the fluoride with borosilicate glass.

6.7.2. Accurately weigh 0.11 ± 0.005 g of solid anhydrous sodium fluoride into a 50-mL polypropylene volumetric flask.

6.7.3. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.7.4. Dilute the solution to volume with reagent water and mix by inversion.

6.7.5. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.7.6. Record information on standard preparation in the QC Laboratory notebook.

6.8. Prepare a standard solution of sulfate ion at approximately 20 mg/mL using solid anhydrous sodium sulfate.

6.8.1. Accurately weigh 1.48 ± 0.03 g of solid anhydrous sodium sulfate into a 50-mL volumetric flask.

6.8.2. Add approximately 30 mL of reagent water and swirl the flask to dissolve the salt.

6.8.3. Dilute the solution to volume with reagent water and mix by inversion.

6.8.4. Transfer the solution to a 60-mL high-density polyethylene bottle and label the bottle with information identifying the standard.

6.8.5. Record information on standard preparation in the QC Laboratory notebook.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically omit one or more analytes from the QC sample as a blank QC for those analytes.

7.2. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size as necessary.

7.3. This step describes the preparation of three approximately 150-mL aliquots of a standard containing bromide, chloride, fluoride, and sulfate anions.

7.3.1. Prepare QC samples containing fluoride in polypropylene (Nalgene) volumetric flasks to avoid loss of fluoride ion due to reaction with borosilicate glass.

7.3.2. Place approximately 400 mL of reagent water into a 500-mL polypropylene volumetric flask.

7.3.3. Spike aliquots of bromide, chloride, fluoride, and sulfate standards made from salts of the anions into the water to reach the desired spike range listed in Table I.

7.3.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.3.5. Divide the QC sample evenly among three 250-mL high-density polyethylene bottles.

7.3.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.4. This step describes the preparation of four 25-mL aliquots of boron standard.

7.4.1. Prepare QC samples containing boron in polypropylene (Nalgene) volumetric flasks to prevent contamination by leaching of borosilicate glass surfaces.

7.4.2. Place approximately 80 mL of reagent water into a 100-mL polypropylene volumetric flask.

7.4.3. Add an aliquot of boron standard solution to the water to reach the desired spike range listed in Table I.

7.4.4. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.4.5. Divide the QC sample evenly among four 60-mL high-density polyethylene bottles.

7.4.6. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 100-mL volumetric flask.

7.5. This step describes the preparation of five 100-mL aliquots of silicon standard.

7.5.1. Prepare QC samples containing silicon in polypropylene (Nalgene) volumetric flasks to prevent contamination by leaching of borosilicate glass surfaces.

7.5.2. Use distilled water to prepare silicon QC samples. Degrading ion-exchange resin used to make deionized water may contaminate the sample with silicon.

7.5.3. Place approximately 400 mL of distilled water into a 500-mL polypropylene volumetric flask.

7.5.4. Add an aliquot of silicon standard to the water to reach the desired spike range for silicon listed in Table I.

7.5.5. Dilute the QC sample to volume with distilled water. Mix by inversion.

7.5.6. Divide the QC sample evenly among five 125-mL high-density polyethylene bottles.

7.5.7. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all five aliquots of a QC sample from the same 500-mL volumetric flask.

7.6. This step describes the preparation of five 100-mL aliquots of phosphorus standard.

7.6.1. Place approximately 400 mL of reagent water into a 500-mL volumetric flask.

7.6.2. Add an aliquot of phosphorus standard solution to the water to reach the desired spike range listed in Table I.

7.6.3. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.6.4. Divide the QC sample evenly among five 125-mL high-density polyethylene bottles.

7.6.5. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 500-mL volumetric flask.

7.7. This step describes the preparation of five 50-mL aliquots of a standard containing calcium, magnesium, potassium, sodium, and lithium.

7.7.1. Place approximately 200 mL of reagent water into a 250-mL volumetric flask.

7.7.2. Add aliquots of the Ca, Mg, K, Na, and Li standard solutions to the water to reach the desired spike range listed in Table I.

7.7.3. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.7.4. Divide the QC sample evenly among five 60-mL high-density polyethylene bottles.

7.7.5. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for all aliquots of a QC sample from the same 250-mL volumetric flask.

7.8. For each QC sample prepared, record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and

CVD databases on the VAX. Record the concentration of the silicon QC sample in terms of both Si and SiO_2.

8. Calculations

8.1. Calculate the concentration of a bromide standard solution made from anhydrous potassium bromide using the following atomic weights and example.

8.1.1. Atomic weight of K = 39.1
Atomic weight of Br = 79.9

8.1.2. If 1.5000 g of KBr is dissolved in 50 mL of reagent water, the bromide concentration in the standard is 20 mg/mL.

$$\frac{\left(\frac{79.9 \text{ g Br}}{119.0 \text{ g KBr}}\right)(1.5000 \text{ g})(1000 \text{ mg/g})}{50 \text{ mL}} = 20 \text{ mg/mL}$$

8.2. Calculate the concentration of a chloride standard solution made from dried sodium chloride using the following atomic weights and example.

8.2.1. Atomic weight of Na = 23.0
Atomic weight of Cl = 35.5

8.2.2. If 1.6500 g of NaCl is dissolved in 50 mL of reagent water, the chloride concentration in the standard is 20 mg/L.

$$\frac{\left(\frac{35.5 \text{ g Cl}}{58.5 \text{ g NaCl}}\right)(1.6500 \text{ g})(1000 \text{ mg/g})}{50 \text{ mL}} = 20 \text{ mg/L}$$

8.3. Calculate the concentration of a fluoride standard solution made from sodium fluoride using the following atomic weights and example.

8.3.1. Atomic weight of Na = 23.0
Atomic weight of F = 19.0

8.3.2. If 0.1110 g of NaF is dissolved in 50 mL of reagent water, the fluoride concentration in the standard is 1004 μg/mL.

$$\frac{\left(\frac{19.0\ g\ F}{42.0\ g\ NaF}\right)(0.1110\ g)\ (1{,}000{,}000\ \mu g/g)}{50\ mL} = 1004\ \mu g/mL$$

8.4. Calculate the concentration of a sulfate standard solution made from anhydrous sodium sulfate using the following atomic weights and example.

8.4.1. Atomic weight of Na = 23.0
Atomic weight of S = 32.1
Atomic weight of O = 16.0

8.4.2. If 1.4750 g of $Na_2\ SO_4$ is dissolved in 50 mL of reagent water, the sulfate concentration in the standard is 20 mg/mL.

$$\frac{\left(\frac{96.1\ g\ SO_4}{142.1\ g\ Na_2SO_4}\right)(1.4750\ g)\ (1000\ mg/g)}{50\ mL} = 20\ mg/mL$$

8.5. Record the concentration of each analyte in a QC sample as μg/L or mg/L.

8.6. Calculate spike concentrations for each analyte in the QC sample as in the following examples.

8.6.1. If 750 μL of a 20-mg/mL Br standard is spiked into 400 mL of reagent water and the solution is diluted to 500 mL, the concentration of Br in the QC sample is 30 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(20\ mg/mL)\ (1\ mL/1000\ \mu L)\ (750\ \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 30\ mg/L$$

8.6.2. If 300 μL of a 1000-μg/mL boron standard is spiked into 80 mL of reagent water and the solution is diluted to 100 mL, the concentration of boron in the QC sample is 3 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(300\mu L)\left(\frac{1\ mg}{1000\ \mu g}\right)}{(100\ mL)\ (1\ L/1000\ mL)} = 3\ mg/L$$

8.6.3. If 900 μL of a 10,000-μg/mL Si standard is spiked into 400 mL of distilled water and the solution is diluted to 500 mL, the concentration of Si in the QC sample is 18 mg/L. The concentration of a Si QC sample is recorded in terms of both Si and SiO_2.

$$\frac{(10{,}000\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(900\ \mu L)\left(\frac{1\ mg}{1000\ \mu g}\right)}{(500\ mL)\ (1\ L/1000\ mL)} = 18\ mg/L$$

The concentration of the QC sample in terms of SiO_2 is calculated from the concentration in terms of Si.

A QC sample with a concentration of 18 mg/L Si has a concentration of 38 mg/L SiO_2.

$$(18\ mg\ Si/L)\left(\frac{60.1\ g\ SiO_2}{28.1\ g\ Si}\right) = 38\ mg\ SiO_2/L$$

Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.6.4. If 250 μL of a 1000-μg/mL P standard is spiked into 400 mL of reagent water and the solution is diluted to 500 mL, the concentration of P in the QC sample is 500 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1000\ \mu g/mL)\left(\frac{mL}{1000\ \mu L}\right)(250\ \mu L)}{(500\ mL)\ (1\ L/1000\ mL)} = 500\ \mu g/L$$

8.6.5. If 150 μL of a 10,000-μg/mL Mg standard is spiked into 200 mL of reagent water and the solution is diluted to 250 mL, the concentration of Mg in the QC sample is 6 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10{,}000\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(150\ \mu L)\left(\frac{1\ mg}{1000\ \mu g}\right)}{(250\ mL)\ (1\ L/1000\ mL)} = 6\ mg/L$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form describing the solid waste is completed and sent to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, the waste is disposed of as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, pickup of the contaminated waste is requested as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants, such as solutions of trace metals, is accumulated in a coated glass bottle in a secondary containment tray and kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-7.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, E. A. Jones, N. L. Koski, B. T. O'Malley, G. H. Brooks "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91, (American Society for Testing and Materials, Philadelphia, Pennsylvania,1992), pp.45-47.

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS FOR WATER AND SOIL (MERCURY BY TCLP) — QC SAMPLE PREPARATION

Analyte: Hg	**Method No.:** QCI200
Matrix: Water	**Spike Range:** 1-4 μg/L
Procedure: Toxicity characteristic leaching procedure (TCLP) followed by cold vapor atomic absorption (CVAA) spectroscopy	**Accuracy and Precision:** 100% ± 5.9% RSD
Effective Date: 09/29/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.7 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified water containing $Cr_2O_7^{=}$ as a stabilizer is spiked with a Hg standard.

1.2. The acidified water quality control (QC) sample may represent the solution resulting from the extraction of Hg from a soil matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure or those sections of the procedure that are applicable.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 5.9% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared from 1989 through 1993 using this procedure and analyzed by cold vapor atomic absorption spectroscopy gave the recoveries found in Table I. The data are published in Source Materials 10.2 through 10.5.

TABLE I. MERCURY SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

	Spike range µg/L	Mean ± std dev (%)	Number of samples
1989	2.0-2.9	88 ± 7	91
	3.0-4.0	100 ± 3	78
1990	1.0-1.9	73 ± 20	6
	2.0-2.9	103 ± 1	24
	3.0-4.0	103 ± 2	96
1991	1.0-2.9	92 ± 19	30
	3.0-4.0	96 ± 11	33
1992	1.0-2.9	94 ± 17	73
	3.0-4.0	96 ± 16	56
1993	1.0-2.9	100 ± 20	102
	3.0-10.0	96 ± 5	85

3. Collection and Storage of Samples

3.1. Low-level Hg solutions must be stabilized to maintain their certified concentration longer than a few hours. Studies of the preservation of dilute Hg solutions (see Source Material 10.1) show that a dilute Hg solution will maintain its concentration for as long as five months if it is preserved with 0.01% $Cr_2O_7^{=}$ and 5% nitric acid and stored in a glass container.

3.2. QC samples are stored in glass bottles at room temperature pending analysis.

3.3. If QC samples for Hg are not used within five months of the date they were made, they are discarded.

4. Apparatus

4.1. Volumetric flasks: 5-, 25-, and 250-mL.

4.2. Auto-pipette: 100- and 1000-µL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Graduated cylinder: 25-mL.

4.5. Bottles: 4-oz, glass, with Teflon-lined screw caps.

4.6. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.7. Spatula.

4.8. Weighing dish: small, polyethylene.

4.9. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (16 M, ultrapure) suitable for trace metal analysis.

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testing and Materials (ASTM) Types I, II, or III and free of interferences with the analytical method.

5.3. Potassium dichromate (analytical reagent-grade).

6. Calibration and Standards

6.1. Spectroscopy-grade Hg standard solution, 10-μg/mL concentration preferred. More concentrated standards, such as those supplied by Spex Industries, Inc., 3880 Park Avenue, Edison, NJ 08820, may be diluted to a Hg concentration of 10 μg/mL.

6.2. A spectroscopy-grade 10-μg/mL Hg standard solution is spiked into acidified water containing $K_2Cr_2O_7$ as a stabilizer for the Hg.

7. Procedure

7.1. Prepare a stabilizing solution for the Hg with a $Cr_2O_7^{=}$ concentration of 50 mg/mL.

7.1.1. Tare a small polyethylene weighing dish on the balance.

7.1.2. Accurately weigh 341 ± 2 mg of analytical-grade $K_2Cr_2O_7$ into the weighing dish.

7.1.3. Use reagent water to quantitatively rinse the $K_2Cr_2O_7$ into a 5-mL volumetric flask and to dilute the solution to volume. Mix by inversion.

7.1.4. Calculate the $Cr_2O_7^{=}$ concentration of the stabilizing solution as in the example in Step 8.1.

7.2. Prepare a 10-μg/mL Hg standard solution from a 1000-μg/mL standard solution.

7.2.1. Place 15 mL of reagent water into a 25-mL volumetric flask.

7.2.2. Add 2.5 mL of ultrapure nitric acid to the water in the flask to produce a final acid concentration of 10% by volume.

7.2.3. Add 50 μL of the stabilizing solution with a $Cr_2O_7^{=}$ concentration of 50 mg/mL to the acidified water to produce a $Cr_2O_7^{=}$ concentration of 0.01% by weight.

CAUTION: The nitric acid and $Cr_2O_7^{=}$ stabilizing solution must be added to the water before the mercury spike to prevent the immediate loss of Hg.

7.2.4. Add 250 μL of a 1000-μg/mL Hg standard solution to the water in the flask.

7.2.5. Dilute to volume with reagent water. Mix by inversion.

7.3. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include a sample of 5% HNO_3 and 0.01% $Cr_2O_7^{=}$ as a blank.

7.4. This procedure describes the preparation of two approximately 100-mL aliquots of a QC sample. QC solutions may be prepared in larger or smaller quantities than described in this procedure. Adjust apparatus size as necessary.

7.5. Place approximately 200 mL of reagent water into a 250-mL volumetric flask.

7.6. Add 12.5 mL of ultrapure nitric acid to the water to produce a final acid concentration of 5% by volume.

7.7. Add 500 μL of the stabilizing solution with a $Cr_2O_7^{=}$ concentration of 50 mg/mL to the acidified water to produce a $Cr_2O_7^{=}$ concentration of 0.01% by weight.

NOTE: The nitric acid and $Cr_2O_7^{=}$ stabilizing solution must be added to the water before the mercury spike to prevent the immediate loss of Hg.

7.8. Spike an aliquot of the 10-μg/mL Hg standard into the acidified water to reach the desired spike range.

7.9. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.10. Divide the QC sample evenly between two 4-oz glass bottles.

7.11. Label each bottle with a QC sample number and store at room temperature pending analysis. The same QC number may be used for both aliquots of a QC sample from the same 250-mL volumetric flask.

7.12. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the $Cr_2O_7^{=}$ concentration of the stabilizing solution using the following atomic weights and example.

8.1.1. Atomic weights: K = 39.1, Cr = 52.0, and O = 16.0.

8.1.2. If 341.0 mg of $K_2Cr_2O_7$ is dissolved in 5 mL of reagent water, the $Cr_2O_7^{=}$ concentration in the stabilizing solution is 50 mg/mL.

$$\frac{\left(\frac{216.0 \text{ g } Cr_2O_7^{=}}{294.2 \text{ g } K_2Cr_2O_7}\right)(341.0 \text{ mg } K_2Cr_2O_7)}{5 \text{ mL}} = 50 \text{ mg } Cr_2O_7^{=}/\text{mL}$$

8.2. Calculate Hg spike concentrations as in the following example.

8.2.1. If 50 μL of a 10-μg/mL Hg standard is diluted to 250 mL in acidified water containing $Cr_2O_7^{=}$ stabilizing solution, the Hg concentration in the sample is 2 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10 \ \mu\text{g/mL})\ (1 \text{ mL}/1000 \ \mu\text{L})\ (50 \ \mu\text{L})}{(250 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 2 \ \mu\text{g/L}$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a coated glass bottle in a secondary containment tray. Keep it segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace metal waste.

9.2.3. Open the bottle only for the period of time necessary to add waste.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-7.

9.2.5. Label a new bottle for further use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. C. Feldman, "Preservation of Dilute Mercury Solutions," *Anal. Chem.* **46**, 99-102 (1974).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. B. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.5. M. A. Gautier, N. L. Koski, E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.6. SPEX Industries, Inc., "Certificate of Analysis for Metals" (SPEX Industries, Inc., Edison, NJ 08820, October 1990).

10.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.8. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation: D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp.45-47.

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN WATER (CN) — QC SAMPLE PREPARATION

Analyte: CN	**Method No.:** QCI210
Matrix: Water	**Spike Range:** 0.1–0.5 mg/L
Procedure: Automated colorimetry	**Accuracy and Precision:** 100% ± 12% RSD
Effective Date: 02/02/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Slightly alkaline blank water is spiked with a commercially prepared cyanide spiking solution.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 12% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared from 1990 through 1993 using this procedure and analyzed by automated colorimetry gave the following recoveries at the 1-σ level. The data are published in Source Materials 10.2 through 10.4.

TABLE I. SPIKE RECOVERY DATA FOR CN

Year	Mean ± std dev	Number of Samples
1990	83 ± 13	11
1991	82 ± 7	23
1992	74 ± 12	40
1993	83 ± 16	48

3. Collection and Storage of Samples

3.1. QC samples are prepared in a volumetric flask and are aliquoted into high-density polyethylene bottles and refrigerated pending analysis.

CAUTION: QC samples must be prepared in an alkaline matrix because cyanide in an acid matrix will release hydrogen cyanide gas, which is extremely hazardous.

4. Apparatus

4.1. Flasks: 250-mL, volumetric, glass, class A.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Pipette: 2-mL, volumetric, class A.

4.5. Bottles: 60-mL, high-density polyethylene.

4.6. Labels printed with QC sample numbers.

4.7. Glass vials: with Teflon-lined caps.

5. Reagents

5.1. Sodium hydroxide (50% or approximately 10 M).

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean water conforming to American Society for Testing and Materials (ASTM) Types I, II, or III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. A commercially prepared cyanide solution is used as a stock solution. National Institute of Standards and Technology (NIST) or Environmental Protection Agency (EPA) traceability is desirable for the stock solution.

6.2. If the manufacturer certifies the concentration of the standard after dilution according to specified instructions, the concentration of the original stock solution must be back-calculated before it is used, taking any dilution instructions into consideration.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include an unspiked water sample made alkaline with 0.02 M NaOH as a blank.

7.2. This procedure describes the preparation of five 50-mL aliquots of QC samples. QC samples may be prepared in larger or smaller quantities than described in this procedure. Adjust apparatus size as necessary.

7.3. Back-calculate the concentration of the undiluted cyanide stock solution. See Step 8.1.

7.4. Place approximately 200 mL of reagent water in a 250-mL volumetric flask.

7.5. Add 500 μL of 50% NaOH to the water to produce a final NaOH concentration of 0.02 M.

CAUTION: Cyanide compounds must not be added to an acidic solution because hydrogen cyanide gas is released and is very hazardous. Work with cyanide solutions in an approved fume hood.

7.6. Spike an aliquot of undiluted cyanide stock solution into the water in the flask to reach the desired spike range.

7.7. Dilute the QC sample to volume with reagent water. Mix by inversion.

7.8. Divide the QC sample evenly among five 60-mL high-density polyethylene bottles.

7.9. Label each bottle with a QC sample number and refrigerate pending analysis. Use the same QC number for all five aliquots of the QC sample.

7.10. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.11. Store the unused portion of the cyanide stock solution in a glass vial with a Teflon-lined cap and refrigerate.

8. Calculations

8.1. Back-calculate the concentration of the undiluted cyanide stock solution as in the following example.

8.1.1. If the concentration of the cyanide stock solution is 0.50 mg/L after dilution of a 10-mL aliquot to 1 L according to instructions, the concentration of the undiluted cyanide sample is calculated as follows:

$$(0.50\ \text{mg/L})\ (1\ \text{L}/10\ \text{mL}) = 0.05\ \text{mg/mL} \quad .$$

8.1.2 The concentration of 0.05 mg/mL is then used to determine the aliquot used to spike the alkaline water sample.

8.2. Record the concentration of CN in the QC sample as mg/L.

8.3. Calculate CN concentrations as in the following example.

8.3.1. If 2 mL of a 0.05-mg/mL CN standard is used to spike 250 mL of alkaline water, the concentration of CN in the sample will be 0.40 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(0.05\ \text{mg/mL})\ (2\ \text{mL})}{(250\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 0.40\ \text{mg/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Step 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste contaminated with cyanide in a glass bottle in a secondary containment tray and keep it in a basic solution segregated from any other liquid waste.

9.2.2. Label the bottle with a hazardous waste label and a label indicating the presence of cyanide. If the bottle is too small to accommodate the hazardous waste label, apply the label to the secondary container.

9.2.3. Open the bottle only for the period of time necessary to add waste to it and keep it in a functioning fume hood whenever it is open.

9.2.4. When the waste is ready for disposal, keep the bottle in the secondary containment tray pending pickup by CST-7.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up a bottle of cyanide-contaminated waste by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. US Environmental Protection Agency, "Instructions for Cyanide Quality Control Sample" (US Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio, February 1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.4. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

TRACE ELEMENTS IN WATER (MINERALS AND NUTRIENTS)

Analyte: Minerals, nutrients	**Method No.:** QCI215
Matrix: Water	**Spike Range:** Dependent on analyte (See Table I).
Procedure: CB, GRAV, CALC, IC, ISE, ACOLR, TITR, FIA	**Accuracy and Precision:** 100% ± 10.4% RSD
Effective Date: 01/01/88	**Authors:** Michael N. Jasperson Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Obtain commercially prepared concentrated standards of minerals and nutrients.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Methods of analysis depend on the analyte. They include conductivity bridge (CB), gravimetry (GRAV), calculation (CALC), ion chromatography (IC), ion-selective electrodes (ISE), automated colorimetry (ACOLR), titration (TITR), and flow injection analysis (FIA).

1.4. The QC spike range is dependent on the analyte. Refer to Table I for the spike ranges.

1.4.1. The typical analytes in a minerals QC sample include conductivity (COND), total dissolved solids (TDS), hardness (HARD), total alkalinity (TALK), Ca, Mg, Na, K, Ci, F, and SO_4.

1.4.2. The typical analytes in a nutrients QC sample include NH_3-N, NO_3-N, PO_4-P, total Kjeldahl nitrogen (TKN), and P.

TABLE I. MINERALS AND NUTRIENTS QC SAMPLE SPIKE RANGES			
QC type	Analyte	Spike range	
Minerals	COND	70 - 900	μmhos/cm
	TDS	60 - 575	mg/L
	HARD	18 - 280	mg/L
	TALK	5 - 120	mg/L
	Ca	15 - 150	mg/L
	Mg	2.0 - 10	mg/L
	Na	15 - 200	mg/L
	K	3 - 20	mg/L
	Cl	5 - 200	mg/L
	F	0.1 - 8	mg/L
	SO_4	5 - 125	mg/L
Nutrients	NH_3-N	0.5 - 20	mg/L
	NO_3-N	0.5 - 35	mg/L
	PO_4-P	0.1 - 5	mg/L
	TKN	0.5 - 20	mg/L
	P	0.05 - 10	mg/L

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 12% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3},$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.1.3. If two pipettes ($P_1 + P_2$) are used to spike the analytes, use the following equation to calculate the pipetting error.

$$R_{M2} = \frac{\sqrt{\sigma_1^2 + \sigma_2^2}}{P_1 + P_2} ,$$

where σ_1 = standard deviation of first pipette,
σ_2 = standard deviation of second pipette,
P_1 = mean of first pipette, and
P_2 = mean of second pipette.

Square R_{M2} and substitute this value in the equation in Step 2.1.2 to calculate the percent RSD for the use of two pipettes.

2.2. Results of analysis by CB, GRAV, CALC, IC, ISE, ACOLR, TITR, and FIA of QC samples prepared from 1991 to 1993 using these procedures are summarized in Table II below.

TABLE II. SPIKE RECOVERY DATA FOR MINERALS AND NUTRIENTS

Analyte	1991 mean ± std dev (%)	N	1992 mean ± std dev (%)	N	1993 mean ± std dev (%)	N
COND	89 ± 13	16	94 ± 8	24	93 ± 5	20
TDS	99 ± 19	16	103 ± 14	22	91 ± 10	20
HARD	111 ± 14	19	110 ± 16	21	102 ± 12	21
Ca	111 ± 11	21	112 ± 4	9	107 ± 11	9
Mg	107 ± 4	20	109 ± 3	9	104 ± 10	9
Na	108 ± 6	23	106 ± 3	9	100 ± 7	9
K	104 ± 6	20	106 ± 8	8	100 ± 8	9
TALK	108 ± 12	19	112 ± 10	22	107 ± 7	20
Cl	125 ± 17	20	96 ± 6	19	92 ± 1	26
F	108 ± 15	18	106 ± 13	19	102 ± 9	21
SO_4	109 ± 15	19	96 ± 9	20	90 ± 4	21
TKN	—		112 ± 0	1	96 ± 5	9
P	—		113 ± 0	1	104 ± 21	9
NH_3-N	90 ± 12	10	99 ± 7	9	84 ± 17	9
NO_3-N	97 ± 5	24	99 ± 5	17	103 ± 5	30
PO_4-P	96 ± 12	19	97 ± 9	22	97 ± 10	18

N = number of samples.

3. Collection and Storage of Samples

3.1. QC samples are prepared in a volumetric flask, aliquoted into high-density polyethylene bottles, and stored at room temperature pending analysis.

4. Apparatus

4.1. Flasks: 1-L and 100-mL, volumetric, glass, class A.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Pipettes: 1- to 10-mL, volumetric, class A.

4.5. Bottles: 60- and 500-mL, high-density polyethylene.

4.6. Labels printed with QC sample numbers.

4.7. Glass vials: with Teflon-lined caps.

5. Reagents

5.1. Sulfuric acid, 3.6 M prepared from 18 M H_2SO_4.

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean water conforming to American Society for Testing and Materials (ASTM) Types I, II, or III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. A commercially prepared concentrate containing the desired analytes is used as a stock solution. National Institute of Standards and Technology (NIST) or Environmental Protection Agency (EPA) traceability is desirable for the concentrates.

6.2. If the manufacturer certifies the concentration of the standard after dilution according to specified instructions, the concentration of the original stock solution must be back-calculated before it is used, taking any dilution instructions into consideration.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the number of samples to be analyzed. Periodically include an unspiked sample of the same matrix as a blank.

7.2. This procedure describes the preparation of two 500-mL aliquots of minerals QC samples. QC samples may be prepared in larger or smaller quantities than described in this procedure. Adjust apparatus size as necessary.

7.2.1. The complete minerals concentrate set may contain multiple vials. Consult the dilution instructions supplied with the concentrates for any special dilution requirements.

7.2.2. Back-calculate the concentration of the undiluted minerals concentrates. See Step 8.1.

7.2.3. Add approximately 800 mL of reagent water to a 1-L volumetric flask.

7.2.4. Spike aliquots of the undiluted minerals concentrates into the water to reach the desired spike range determined from Table I.

7.2.5. Dilute the sample to volume with reagent water.

7.2.6. Mix by inversion.

7.2.7. Divide the sample evenly into two 500-mL high-density polyethylene bottles.

7.2.8. Label each bottle with a QC number. The same QC number may be used for each aliquot of the QC sample.

7.3. This procedure describes the preparation of two 50-mL aliquots of nutrients QC samples. QC samples may be prepared in larger or smaller quantities than described in this procedure. Adjust apparatus size as necessary.

7.3.1. The complete nutrients concentrate set may contain multiple vials. Consult the dilution instructions supplied with the concentrates for any special dilution requirements.

7.3.2. Back-calculate the concentration of the undiluted nutrients concentrate. See Step 8.1.

7.3.3. Add approximately 80 mL of reagent water to a 100-mL volumetric flask.

7.3.4. Add 1000 μL of 3.6 M H_2SO_4 to the water to produce a final pH <2.

7.3.5. Spike aliquots of the undiluted nutrients concentrates into the acidified water to reach the desired spike range determined from Table I.

7.3.6. Dilute the sample to volume with reagent water.

7.3.7. Mix by inversion.

7.3.8. Divide the sample evenly into two 60-mL high-density polyethylene bottles.

7.3.9. Label each bottle with a QC number. The same QC number may be used for each aliquot of the QC sample.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.5. Store unused portions of the undiluted concentrates of minerals and nutrients in glass vials with Teflon-lined caps and refrigerate.

8. Calculations

8.1. Back-calculate the concentration of the undiluted minerals and nutrients concentrates as in the following example.

8.1.1. If the concentration of Ca in a minerals sample is 20.0 mg/L after the dilution of a 10-mL aliquot to 1 L according to the supplied dilution instructions, the concentration of Ca in the undiluted minerals concentrate is 2.0 mg/mL.

$$20.0\ \text{mg/L} \times \frac{1\ \text{L}}{10\ \text{mL}} = 2.0\ \text{mg/mL}$$

8.1.2. Use the concentration of 2.0 mg/mL to determine the aliquot needed to spike the QC sample.

8.2. Calculate analyte concentrations in the minerals QC sample as in the following example.

8.2.1. If 8.0 mL of a minerals concentrate containing 2.0 mg/mL Ca is used to spike 1 L of reagent water, the concentration of Ca in the QC sample will be 16.0 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{2.0\ \text{mg/mL} \times 8.0\ \text{mL}}{1\ \text{L}} = 16.0\ \text{mg/L}$$

8.3. Calculate analyte concentrations in the nutrients QC sample as in the following example.

8.3.1. If 300 μL of a nutrients concentrate with 200 mg/L NH_3-N is used to spike 100 mL of acidified water, the concentration of NH_3-N in the QC sample will be 0.60 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{200\ \text{mg/L} \times \dfrac{1\ \text{L}}{1 \times 10^6\ \mu\text{L}} \times 300\ \mu\text{L}}{100\ \text{mL} \times \dfrac{1\ \text{L}}{1000\ \text{mL}}} = 0.60\ \text{mg/L}$$

8.4. Record the concentration of analytes in a minerals QC sample as mg/L, except for COND, which is recorded in μmhos/cm.

8.5. Record the concentration of analytes in a nutrients QC sample as mg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, the appropriate paperwork is completed on a case-by-case basis.

9.1.2.1. A Waste Profile Form (WPF) describing the solid waste is completed and sent to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Liquid waste containing hazardous contaminants (such as solutions of trace metals) is accumulated in a coated glass bottle in a secondary containment tray and is kept segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. The bottle is labeled with a hazardous waste label and a label indicating its use for trace-metal waste.

9.2.3. The bottle is opened only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-7.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. B. Brooks, W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Standard Specification for Reagent Water," in *Annual Book of ASTM Standards*, Vol. 11.01, Designation : D1193-91 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1992), pp. 45-47.

TRACE ELEMENTS IN WATER (NO_2-N) — QC SAMPLE PREPARATION

Analyte: NO_2-N	**Method No.:** QCI220
Matrix: Water	**Spike Range:** 0.1–1.0 mg/L
Procedure: Flow Injection Colorimetry	**Accuracy and Precision:** 100% ± 5.8% RSD
Effective Date: 10/22/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Sodium nitrite is weighed into a volumetric flask.

1.2. Immediately before use, the weighed salt is dissolved in reagent water and the solution is used to spike reagent water for use as a quality control (QC) sample.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the error of the standard and on the error associated with use of the pipette, balance, and volumetric flask. A relative standard deviation (RSD) of 5.8% at the 1-σ level has been calculated for the error of the standard and for the spiking, weighing, and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,

M4 = pipette error, and
M5 = second dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2}$$

where $R^2{}_M$ = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2 + R_{M5}^2} \times 100$$

where S_{D_T} = RSD (% error),
$R^2{}_{M1}$ = relative variance of standard,
$R^2{}_{M2}$ = relative variance of balance,
$R^2{}_{M3}$ = relative variance of volumetric flask,
$R^2{}_{M4}$ = relative variance of pipette,
$R^2{}_{M5}$ = relative variance of second volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared from 1990 through 1993 using this procedure and analyzed by flow injection colorimetry gave the following recoveries at the 1-σ level. The data are published in Source Materials 10.1. through 10.3.

TABLE I. SPIKE RECOVERY DATA FOR NO_2-N IN WATER

Year	Mean ± std dev	Number of Samples
1990	96 ± 15	4
1991	99 ± 29	5
1992	99 ± 15	5
1993	95 ± 17	5

3. Collection and Storage of Samples

3.1. Aliquots of crystalline sodium nitrite to be diluted and used to prepare QC samples are stored at room temperature pending analysis.

3.2. A water solution of sodium nitrite cannot be stored as a QC sample because nitrite in solution is readily oxidized to nitrate by the oxygen in the air.

4. Apparatus

4.1. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.2. Flasks: 10- and 100-mL, volumetric.

4.3. Spatula.

4.4. Auto-pipette: 100-μL, Rainin or equivalent.

4.5. Pipette tips: disposable.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Sodium nitrite (analytical reagent-grade, crystalline).

5.2. Water. In this procedure, water referred to as "reagent water" is understood to mean reagent water conforming to American Society for Testin and Materials (ASTM) Type I, II, or III and free of interferences with the analytical method.

6. Calibration and Standards

6.1. Dissolve 10-100 mg of analytical-grade crystalline sodium nitrite in 10 mL of reagent water immediately before use.

6.2. Spike 50 μL of the sodium nitrite solution into 100 mL of reagent water to prepare the QC sample.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 100-mL QC sample.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3. Accurately weigh between 10 and 100 mg of sodium nitrite into a 10-mL volumetric flask.

7.4. Stopper the flask and label it with a QC sample number. Store the sample at room temperature pending final dilution by the analyst.

7.5. The sodium nitrite should be dissolved and diluted as close to time of analysis as possible to prevent loss of the QC sample through oxidation of nitrite to nitrate.

7.6. Place a label on the flask with instructions to the analyst for completion of the QC sample as described below.

7.6.1. Dissolve the sodium nitrite in reagent water in the 10-mL volumetric flask. Dilute the solution to volume with reagent water. Mix by inversion.

7.6.2. Place approximately 90 mL of reagent water in a 100-mL volumetric flask.

7.6.3. Spike 50 μL of the sodium nitrite solution from the 10-mL flask into the water in the 100-mL flask.

7.6.4 Dilute the QC sample in the 100-mL flask to volume with reagent water. Mix by inversion.

7.6.5. Analyze the QC sample immediately after preparation, using the same QC sample number that is on the 10-mL volumetric flask.

7.7. Calculate the concentration of the QC sample as the concentration after final dilution in the 100-mL flask by the analyst.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of NO_2-N in the QC sample as mg/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. Atomic weights: Na = 23, N = 14, and O = 16. The ratio of the atomic weight of N in $NaNO_2$ to the molecular weight of $NaNO_2$ is 14:69.

8.2.2. If 55.8 mg of sodium nitrite is dissolved in 10 mL of reagent water, the NO_2-N concentration in the resulting stock solution will be 1.13 mg/mL.

$$\frac{(55.8 \text{ mg } NaNO_2)\ (14 \text{ mg N}/69 \text{ mg } NaNO_2)}{10 \text{ mL}} = 1.13 \text{ mg N/mL} \ .$$

8.2.3. If 50 μL of the $NaNO_2$ stock solution with a NO_2-N concentration of 1.13 mg/mL is used to spike 100 mL of reagent water, the final concentration of NO_2-N in the QC sample will be 0.57 mg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1.13 \text{ mg N/mL})\ (1 \text{ mL}/1000\ \mu\text{L})\ (50\ \mu\text{L})}{(100 \text{ mL})\ (1 \text{ L}/1000 \text{ mL})} = 0.57 \text{ mg/L} \ .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Solid waste contaminated with hazardous chemicals above the level of concern is not normally generated during the routine preparation of QC samples for analysis for inorganic contaminants.

9.1.2. If a solid waste is generated that may be contaminated at a level of concern, complete the appropriate paperwork on a case-by-case basis.

9.1.2.1. Complete a Waste Profile Form (WPF) describing the solid waste and send to Waste Management (CST-7) for review.

9.1.2.2. If CST-7 determines that the solid waste is contaminated below the level of concern, dispose of the waste as ordinary laboratory trash.

9.1.2.3. If CST-7 determines that the solid waste is contaminated above the level of concern, request pickup of the contaminated waste as described in Sec. 9.3.

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing hazardous contaminants (such as solutions of trace metals) in a coated glass bottle in a secondary containment tray and keep it segregated from liquid waste contaminated with organic or radioactive substances or cyanide.

9.2.2. Label the bottle with a hazardous waste label and a label indicating its use for trace metal waste.

9.2.3. Open the bottle only for the period of time necessary to add waste to it.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-7.

9.2.5. Label a new bottle for further use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up solid waste or a full bottle of liquid waste containing trace metals by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992, " Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

FORMALDEHYDE ON TUBES — QC SAMPLE PREPARATION

Analyte: Formaldehyde	**Method No.:** QCO100
Matrix: Orbo-24 sorbent beads	**Spike Range:** 4–60 μg/sample
Procedure: Analysis by gas chromatography with a mass selective detector	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 05/08/91	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution of formaldehyde in water.

1.2. Spike the stock solution onto XAD-2 beads coated with 2-(hydroxymethyl)piperidine in an autosampler vial.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. The formaldehyde in the reagent solution is assigned a 100% purity and the assumption is made that M1 = 1. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the error of the standard and for the spiking, weighing, and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error, and
M4 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
X = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation. The formaldehyde in the reagent solution is assigned a 100% purity and the assumption is made that $R^2_{M1} = 0$.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.2. Analysis by gas chromatography of QC samples prepared between June 1991 and February 1993 using this procedure (N = 24) gave a mean recovery of 92% ± 14% at the 1-σ level. The data are published in Source Material 10.1.

3. Collection and Storage of Samples

3.1. The beads are transferred to an autosampler vial before spiking because the static charge that develops on the wetted beads would prevent quantitative transfer of the beads from a sorbent tube into an extraction vessel.

3.2. A study performed in 1991 and 1992 indicates that spiked samples are stable for at least 5 months stored in a freezer at -4°C.

4. Apparatus

4.1. Volumetric flask: 5-mL, class A, glass.

4.2. Pipettes: Pasteur, disposable, glass.

4.3. Bulbs: rubber, to fit Pasteur pipettes.

4.4. Syringe: gas-tight, 10-, 25-, and 50-μL.

4.5. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.6. Sorbent tube: 150-mg primary bed, 75-mg backup bed, XAD-2 coated with 2-(hydroxymethyl)piperidine, such as Orbo-24, to absorb formaldehyde.

4.7. File: triangular.

4.8. Tweezers.

4.9. Autosampler vials: 11- × 30-mm vials with crimp-top caps and silicon cap liners with Teflon face.

4.10. Portable crimper for sealing caps on autosampler vials.

4.11. Teflon tape.

4.12. Drying oven: capable of sustaining 100–150°C.

4.13. Labels: printed with QC sample numbers.

5. Reagents

5.1. Distilled water. Use water that has not been run through plastic tubing or stored in plastic holding vessels because phthalates may leach from plastics and contaminate the sample.

6. Calibration and Standards

6.1. Formaldehyde (analytical-grade). The reagent will be approximately 37.4 wt % formaldehyde in water. The percent purity must be included in the calculations for the concentration of the stock solution. See Step 8.2.

CAUTION: Formaldehyde is an Occupational Health and Safety Administration (OHSA)-regulated carcinogen. Work with formaldehyde in an approved fume hood.

6.2. Add approximately 4 mL of distilled water to a 5-mL volumetric flask and stopper the flask.

6.3. Place the stoppered flask on an analytical balance and tare the balance.

6.4. Calculate the volume of formaldehyde solution needed to make a stock solution containing 5–10 mg of formaldehyde in 5 mL of solution. Include the percent purity of the formaldehyde solution in the calculations. See Step 8.1.

6.5. Using a syringe, add the formaldehyde to the flask just above the surface of the water. Stopper the flask and record the mass and volume of formaldehyde solution added.

6.6. Dilute the solution to volume with distilled water.

6.7. Mix by inversion.

6.8. Label the flask with information identifying the standard.

6.9. Wrap Teflon tape around the stopper of the volumetric flask and store the solution in the refrigerator.

7. Procedure

7.1. Cleaning of glassware.

7.1.1. Wash volumetric flasks with detergent and rinse them with hot tap water and methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use with formaldehyde.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for a minimum of 10 min.

7.3. Preparation of QC samples.

7.3.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.2. This procedure describes the preparation of two QC samples using the beads from one sorbent tube.

CAUTION: Formaldehyde is an OSHA-regulated carcinogen. Work with formaldehyde in an approved fume hood.

7.3.2.1. Remove the flask of formaldehyde stock solution from the refrigerator and allow it to reach room temperature.

7.3.2.2. Open the formaldehyde sorbent tube.

7.3.2.3. Remove the glass wool plugs with tweezers and divide the beads from both beds evenly between two autosampler vials.

7.3.3. Using a gas-tight syringe, spike an aliquot of the formaldehyde stock solution onto the beads to reach the desired spike range. Avoid wetting the vial walls.

7.3.4. Seal a cap onto the vial. Wrap Teflon tape over and around the cap.

7.3.5. Label the vial with a QC sample number.

7.3.6. Return the flask containing the formaldehyde stock solution to the refrigerator.

7.3.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.3.8. Store the samples in a freezer pending analysis. Samples are stable for at least 5 months stored at -4°C.

8. Calculations

8.1. Calculate the volume of formaldehyde solution to dilute to 5 mL as in the following example.

8.1.1. The desired weight spike range for 5 mL of formaldehyde stock solution is 5–10 mg of formaldehyde.

8.1.2. Formaldehyde reagent is approximately 37.4 wt % formaldehyde in water. The density of a 37.4 wt % solution is 1.083 mg/μL.

8.1.3. Divide the weight spike range by the density and the purity of the formaldehyde reagent to determine the volume spike range of formaldehyde reagent to use in 5 mL of stock solution.

$$\frac{5\ \text{mg}}{(1.083\ \text{mg}/\mu\text{L})\ (0.374)}\ \text{to}\ \frac{10\ \text{mg}}{(1.083\ \text{mg}/\mu\text{L})\ (0.374)} = 12.3\ \text{to}\ 24.7\ \mu\text{L}\ .$$

8.1.4. Dilute 12.3–24.7 μL of 37.4 wt % formaldehyde reagent to 5 mL to reach the desired concentration range of 1–2 mg/mL formaldehyde in the stock solution.

8.2. Calculate the concentration of formaldehyde in the stock solution as in the following example.

8.2.1. If 20 μL of 37.4 wt % formaldehyde reagent, weighing 21.7 mg, is diluted to 5 mL with distilled water, the concentration of formaldehyde in the stock solution is 1.62 mg/mL.

$$\frac{(21.7\ \text{mg})\ (0.374)}{5\ \text{mL}} = 1.62\ \text{mg/mL}\ .$$

8.3. Calculate the concentration of formaldehyde in the QC sample as in the following example.

8.3.1. If 15 μL of a stock solution containing 1.62 mg/mL of formaldehyde is spiked onto sorbent beads in an autosampler vial, the concentration of formaldehyde in the sample is 24 μg/sample.

$$\frac{\left(\frac{1.62\ \text{mg}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(15\ \mu\text{L})}{\text{sample}} = 24\ \mu\text{g/sample}\ .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record the formaldehyde concentration in the QC sample in μg/sample.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste that has been contaminated with organic compounds (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape, and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, out-of-date stock solutions, excess QC samples, and incorrectly spiked samples) in a covered metal can in a secondary containment tray and keep it segregated from PCB-contaminated liquid waste and waste that does not contain organic compounds.

9.2.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the can is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.5. Label a new can for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full container of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. Reference the current WPF describing the waste on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (). Where a section heading is marked the entire section has been revised.

HERBICIDES ON SOIL — QC SAMPLE PREPARATION

Analyte: Herbicides	**Method No.:** QCO110
Matrix: Soil	**Spike Range:** 60–1000 μg/kg
Procedure: Analysis by solid phase extraction followed by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** 100% ± 4.4% RSD
Effective Date: 01/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in methanol of herbicides selected primarily from the list in Section 6, Table II.

1.2. Prepare a 1:10 dilution in methanol of the stock solution.

1.3. Spike the 1:10 dilution directly onto blank soil.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, volumetric flask, and balance. A relative standard deviation (RSD) of 4.4% at the 1-σ level has been calculated for the error of the standard and for the spiking and weighing process based on the following function:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7} ,$$

where D = calculated result,
M1 = standard error,
M2 = first weighing error,
M3 = first dilution error,
M4 = first spiking error,
M5 = second dilution error,
M6 = second spiking error, and
M7 = second weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6} + R^2_{M7}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of first balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of second balance, and
100 = factor to convert to percentage.

2.2. Analysis by solid phase extraction and gas chromatography of QC samples (N = 5) prepared using this procedure since October 1990 are summarized in Table I below. The data are published in Source Materials 10.1 through 10.3.

TABLE I. HERBICIDES-ON-SOIL SPIKE RECOVERY DATA		
Compound	% Recovery Mean ± RSD	(N)
2,4-D	82 ± 18	(5)
Silvex	94 ± 24	(5)
2,4,5-T	93 ± 14	(4)

3. Collection and Storage of Samples

3.1. The blank soil matrix and the spiked samples should be stored in glass bottles fitted with Teflon-lined lids. Avoid using plastic containers and lids because phthalates, which are semivolatile compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for the analysis of herbicides on soil is 7 days.

4. Apparatus

4.1. Volumetric flasks: 5- and 100-mL, class A, glass.

4.2. Syringes: gas-tight, 50-, 100-, 250-, 500-, and 1000-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Bulbs: rubber, to fit Pasteur pipettes.

4.6. Bottles: 2-oz, amber, glass, with Teflon-lined caps.

4.7. Vials: 1.5-mL, amber, glass.

4.8. Caps: open-top to fit vials.

4.9. Septa: Teflon/silicone discs to fit open-top caps.

4.10. Teflon tape.

4.11. Bottles: 2-oz, glass, with Teflon-lined caps.

4.12. Analytical balance: 200-g minimum capacity, 0.1-mg accuracy.

4.13. Laboratory oven: capable of sustaining 100–150°C.

4.14. Labels: printed with QC sample numbers.

5. Reagents

5.1. Soil: a clean, dry 50-g aliquot is required for each sample.

5.1.1. A suitable soil does not contain the analyte of interest and presents few interferences to the analytical method.

5.1.2. Blank soil heated to nominally 100°C for 5 h and stored in glass is used as a sample matrix.

5.2. Methanol (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade herbicides selected primarily from the list in Table II. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19387). Use the free acid form of the herbicides, not the methyl esters, since the compounds are esterified during the analytical procedure.

6.1.1. Determine the desired concentration of each analyte in the stock solution. Typical ranges for the concentrated stock solution are listed in Table II. The concentration of an analyte in the stock solution may be varied depending on the desired spike range for the analyte in the QC sample.

TABLE II. TYPICAL CONCENTRATION RANGES FOR QC SAMPLES AND CONCENTRATED STOCK SOLUTIONS FOR VARIOUS HERBICIDES

Compound	CAS number	QC samples µg/g	Concentrated stock mg/mL
2,4-D	94757	0.30–0.90	1.2–3.0
Silvex	93721	0.08–0.24	0.4–0.8
2,4,5-T	93765	0.14–0.42	0.6–2.4
Dinoseb	88857	0.06–0.18	0.3–0.8

2,4-DB	94826	0.60–0.80	1.2–5.0
Dichlorprop	120365	0.35–1.00	1.4–5.0
Dicamba	1918009	0.18–0.54	0.8–3.0
Dalapon	75990	0.24–1.00	1.4–4.0

6.1.2. Add the desired amount of a solid herbicide analyte to a clean, tared, 100-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.3. Add approximately 80 mL of methanol to the flask and swirl it to dissolve all the analytes.

6.1.4. Dilute the solution to volume with methanol.

6.1.5. Mix by inversion.

6.1.6. Transfer the stock to 2-oz amber bottles with Teflon-lined lids. Cap the bottles and wrap Teflon tape around the caps.

6.1.7. Label the bottles with information identifying the standard.

6.1.8. The stock is stable for at least 3 months stored in a refrigerator.

6.2. Prepare a 1:10 dilution of the stock solution.

6.2.1. Remove the concentrated stock from the refrigerator and allow it to reach room temperature before making a dilution.

6.2.2. Add approximately 4 mL of methanol to a clean 5-mL volumetric flask.

6.2.3. Using a gas-tight syringe, add 500 μL of the stock solution just above the surface of the methanol.

6.2.4. Dilute the solution to volume with methanol.

6.2.5. Mix by inversion.

6.2.6. Transfer the dilution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the cap.

6.2.7. Label the vials with information identifying the standard.

6.2.8. Return the concentrated stock to the refrigerator.

6.2.9. The dilution is stable for at least 3 months stored in a refrigerator.

7. Procedure

7.1. Cleaning of glassware.

7.1.1. Wash volumetric flasks with detergent and rinse them with hot tap water and methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use with herbicide analytes.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for a minimum of 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a herbicide-on-soil QC sample using 50 g of blank soil and a 2-oz glass bottle.

7.3.2. Remove a vial of 1:10 dilution of herbicide stock standard from the refrigerator and allow it to reach room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.3. Accurately weigh 50 g of blank soil into a 2-oz glass bottle with a Teflon-lined lid. Record the mass of soil on the bottle with a felt-tipped pen for reference by the analyst.

7.3.4. Using a gas-tight syringe, spike an aliquot of the standard onto the surface of soil to reach the desired spike range. Blank QC samples may be made by spiking methanol onto the soil. The analyst will use the entire sample.

7.3.5. Cap the bottle and label it with a QC sample number.

7.3.6. Return the 1:10 dilution of the standard to the refrigerator.

7.3.7. Refrigerate the QC sample pending analysis. The maximum holding time for herbicides on soil QC samples is 7 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of each analyte in the stock solution as in the following example.

8.1.1. If 150.0 mg of 2,4-D is dissolved in 100.0 mL of methanol, the concentration of 2,4-D in the stock solution is 1.50 mg/mL.

$$\frac{150\ \text{mg}}{100\ \text{mL}} = 1.50\ \text{mg/mL}\ .$$

8.2. Calculate the concentration of each analyte in the 1:10 dilution of the stock solution as in the following example.

8.2.1. If 500 µL of a stock solution containing 1.50 mg/mL of 2,4-D is diluted to 5 mL with methanol, the concentration of 2,4-D in the 1:10 dilution is 150 µg/mL.

$$\frac{\left(\frac{1.50\ \text{mg}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(500\ \mu\text{L})\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{5\ \text{mL}} = 150\ \mu\text{g/mL}\ .$$

8.3. Calculate the concentration of each analyte in the QC sample as in the following example.

8.3.1. If 170 µL of a 1:10 stock dilution containing 150 µg/mL of 2,4-D is spiked onto 50.0000 g of blank soil, the concentration of 2,4-D in the QC sample is 510 µg/kg.

$$\frac{\left(\frac{150\ \mu\text{g}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(170\mu\text{L})}{50.0000\ \text{g}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)} = 510\ \mu\text{g/kg}\ .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.3. Record analyte concentrations in the QC sample in μg/kg or μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) contaminated with organic compounds in a covered metal can lined with a plastic bag and keep it segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the sealed bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste to it.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) in a covered metal can in a secondary containment tray.

9.2.1.1. Keep liquid waste containing organic compounds segregated from PCB-contaminated liquid waste and from waste that does not contain organic compounds.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the can is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.5. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB contaminated.

9.2.2.2. Label the bottle with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the bottle only for the time necessary to add vials.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full container of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

HERBICIDES IN WATER — QC SAMPLE PREPARATION

Analyte: Herbicides	**Method No.:** QCO120
Matrix: Water	**Spike Range:** 0.6–24 μg/L
Procedure: Analysis by solid phase extraction followed by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** 100% ± 4.4% RSD
Effective Date: 04/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.2 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in methanol of herbicides selected primarily from the list in Sec. 6, Table I.

1.2. Prepare a 1:50 dilution in methanol of the stock solution.

1.3. Spike the 1:50 dilution directly into distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the balance, microsyringe, and volumetric flask. A relative standard deviation (RSD) of 4.4% at the 1-σ level has been calculated for standard preparation and for the weighing, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7},$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = first dilution error,
M4 = first pipette error,

M5 = second dilution error,
M6 = second pipette error, and
M7 = third dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6} + R^2_{M7}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of third volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by solid phase extraction and gas chromatography of QC samples (N = 2) prepared using this procedure in 1992 gave a mean recovery of 99% ± 10% at the 1-σ level. The data are published in Source Material 10.1.

3. Collection and Storage of Samples

3.1. Distilled water is used as the blank matrix for spiking. Use water that has not been run through plastic tubing or stored in plastic holding vessels because phthalates, which are semivolatile organic compounds, may leach from plastics and contaminate the samples.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for herbicides-in-water analysis is 7 days.

4. Apparatus

4.1. Volumetric flasks: 5-, 100-, and 1000-mL, class A, glass.

4.2. Syringes: gas-tight, 50-, 100-, 250-, 500-, and 1000-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Bulbs: rubber, to fit Pasteur pipettes.

4.6. Bottles: 2-oz, amber, glass, with Teflon-lined caps.

4.7. Vials: 1.5-mL, amber, glass.

4.8. Caps: open-top to fit vials.

4.9. Septa: Teflon/silicone discs to fit open-top caps.

4.10. Teflon tape.

4.11. Bottles: 1-L, wide-mouth, amber, glass, precleaned, with Teflon-lined lids.

4.12. Analytical balance: 200-g minimum capacity, 0.1-mg accuracy.

4.13. Drying oven: capable of sustaining 100-150°C.

4.14. Labels: printed with QC sample numbers.

5. Reagents

5.1. Methanol (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade herbicides selected primarily from the list in Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19387). Use the free acid form of the herbicides, not the methyl esters, since the compounds are esterified during the analytical procedure.

6.1.1. Determine the desired concentration of each analyte in the stock solution. Typical ranges for the concentrated stock solution are listed in Table I. The concentration of an analyte in the stock solution may be varied depending on the desired spike range for the analyte in the QC sample.

TABLE I. TYPICAL CONCENTRATION RANGES FOR QC SAMPLES AND CONCENTRATED STOCK SOLUTIONS FOR VARIOUS HERBICIDES

Compound	CAS number	QC samples µg/L	Concentrated stock mg/mL
2,4-D	94757	1.6–6.0	1.2–3.0
Silvex	93721	0.6–2.4	0.4–0.8
2,4,5-T	93765	2.0–8.0	0.6–2.4
Dinoseb	88857	0.8–3.0	0.3–0.8
2,4-DB	94826	6.0–24	1.2–5.0
Dichlorprop	120365	6.0–24	1.4–5.0
Dicamba	1918009	2.5–10	0.8–3.0
Dalapon	75990	6.0–24	1.4–4.0

6.1.2. Add the desired amount of a solid herbicide analyte to a clean, tared, 100-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.3. Add approximately 80 mL of methanol to the flask and swirl it to dissolve all the analytes.

6.1.4. Dilute the solution to volume with methanol.

6.1.5. Mix by inversion.

6.1.6. Transfer the stock to 2-oz amber bottles with Teflon-lined lids. Cap the bottles and wrap Teflon tape around the caps.

6.1.7. Label the bottles with information identifying the standard.

6.1.8. The stock is stable for at least 3 months stored in a refrigerator.

6.2. Prepare a 1:50 dilution of the stock solution.

6.2.1. Remove the concentrated stock from the refrigerator and allow it to reach room temperature before making a dilution.

6.2.2. Add approximately 4 mL of methanol to a clean 5-mL volumetric flask.

6.2.3. Using a gas-tight syringe, add 100 μL of the stock solution just above the surface of the methanol.

6.2.4. Dilute the solution to volume with methanol.

6.2.5. Mix by inversion.

6.2.6. Transfer the dilution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the cap.

6.2.7. Label the vials with information identifying the standards.

6.2.8. Return the concentrated stock to the refrigerator.

6.2.9. The dilution is stable for at least 3 months stored in a refrigerator.

7. Procedure

7.1. Cleaning of glassware.

7.1.1. Wash volumetric flasks with detergent and rinse them with hot tap water and methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use with herbicide analytes.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for a minimum of 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a 1-L herbicides-in-water QC sample in an amber glass jar.

7.3.2. Remove a vial of 1:50 dilution of herbicide stock standard from the refrigerator and allow it to reach room temperature. Do not let the vial

sit out at room temperature for longer than 2 h before spiking the QC sample.

7.3.3. Fill a 1000-mL volumetric flask nearly to the volume mark with distilled water that has not been stored in a plastic container.

7.3.4. Using a gas-tight syringe, spike an aliquot of the 1:50 dilution beneath the surface of the water to reach the desired spike range. Blank QC samples may be made by spiking methanol instead of the stock dilution.

7.3.5. Dilute the sample to volume with distilled water. Mix by inversion.

7.3.6. Transfer the sample to a 1-L amber glass bottle with a Teflon-lined lid.

7.3.7. Cap the bottle and label it with a QC sample number.

7.3.8. Refrigerate the sample pending analysis. The maximum holding time for a herbicides-in-water QC sample is 7 days.

7.3.9. Return the vial of 1:50 dilution of herbicide stock standard to the refrigerator.

7.3.10. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of each analyte in the stock solution as in the following example.

8.1.1. If 150.0 mg of 2,4-D is dissolved in 100.0 mL of methanol, the concentration of 2,4-D in the stock solution is 1.5 mg/mL.

$$\frac{150 \text{ mg}}{100 \text{ mL}} = 1.5 \text{ mg/mL} .$$

8.2. Calculate the concentration of each analyte in the 1:50 dilution of the stock solution as in the following example.

8.2.1. If 100 μL of a stock solution containing 1.5 mg/mL of 2,4-D is diluted to 5 mL with methanol, the concentration of 2,4-D in the 1:50 dilution is 30 μg/mL.

$$\frac{\left(\frac{1.5\ \text{mg}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(100\ \mu\text{L})\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{5\ \text{mL}} = 30\ \mu\text{g/mL}\ .$$

8.3. Calculate the concentration of each analyte in the QC sample as in the following example.

8.3.1. If 125 μL of 1:50 stock dilution containing 30 μg/mL of 2,4-D is spiked into 1L of distilled water, the concentration of 2,4-D in the QC sample is 3.75 μg/L.

$$\frac{\left(\frac{30\ \mu\text{g}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(125\ \mu\text{L})}{1\ \text{L}} = 3.75\ \mu\text{g/L}\ .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record analyte concentrations of the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) contaminated with organic compounds in a covered metal can lined with a plastic bag and keep it segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the sealed bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste to it.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) in a covered metal can in a secondary containment tray.

9.2.1.1. Keep liquid waste containing organic compounds segregated from PCB-contaminated liquid waste and from waste that does not contain organic compounds.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the can is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.5. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB contaminated.

9.2.2.2. Label the bottle with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the bottle only for the time necessary to add vials.

9.2.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new bottle for future use.

9.3. Waste pickup.

9.3.1. Request pickup by CST-17 of a full container of waste contaminated with organic compounds using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Material

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒). Where a section heading is marked, the entire section has been revised.

ORGANIC COMPOUNDS ON TUBES AND BADGES — QC SAMPLE PREPARATION

Analyte: Organic compounds	**Method No.:** QCO130
Matrix: Charcoal tubes and organic vapor monitor badges **Procedure:** Gas chromatography with mass spectrometry (GCMS)	**Spike Range:** Charcoal tube: 30-300 μg/tube Organic vapor monitor: 30-100 μg/sample NIOSH-PAT study: 0.2-2 mg/tube **Accuracy and Precision:** 100% ± 8.2% RSD
Effective Date: 03/05/84	**Author:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.8 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution of organic compounds of interest selected primarily from Table I (found at the end of this procedure) in a solvent compatible with the analytical extraction method.

1.2. The solvent most commonly used is carbon disulfide. Methylene chloride is also used frequently. If possible, the solvent should have a shorter chromatographic retention time than the organic compounds of interest in the solution.

1.3. Spike the stock directly into a charcoal tube or onto the filter paper inside an organic vapor monitor (OVM) badge.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 8.2% has been calculated for the error of the standard and for spiking, weighing, and dilution, based on the following:

$$D = \frac{M1 \times M2 \times M4}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error, and
M4 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} \times R^2_{M3} \times R^2_{M4}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.2. Analyses by GCMS of QC samples prepared between 1984 and 1989 using this procedure are found in Table II below. The data are published in Source Materials 10.1 to 10.7.

TABLE II. CHARCOAL TUBE AND BADGE SPIKE RECOVERY DATA

Compound	Year	Mean ± std dev (%)	(N)
Benzene	1984	106 ± 2	4
	1985	133 ± 1	3
	1986	86 ± 3	3
	1987	61 ± 8	3
	1988	83 ± 6	4
	1989	118 ± 4	3
Carbon tetrachloride	1984	98 ± 9	4
	1985	103 ± 4	3
	1986	97 ± 2	5
	1987	110 ± 11	7
	1988	100 ± 6	8
	1989	90 ± 12	12
Cellosolve acetate	1986	95 ± 5	3
	1987	102 ± 4	3
	1988	102 ± 2	4
Chloroform	1984	116 ± 9	8
	1985	101 ± 4	3
	1986	95 ± 3	3
	1987	88 ± 5	4
	1988	99 ± 12	4
	1989	109 ± 2	4
1,2-Dichloroethane	1984	91 ± 12	4
	1985	99 ± 3	6
	1986	130 ± 40	2
	1987	95 ± 5	7
	1988	99 ± 2	7
	1989	94 ± 6	11
p-Dioxane	1985	94 ± 4	6
	1986	101 ± 5	3
	1988	100 ± 1	4
Methyl chloroform	1984	106 ± 7	8
Methyl ethyl ketone	1984	93 ± 8	3
Trichloroethane	1989	89 ± 4	4

TABLE II. CHARCOAL TUBE AND BADGE SPIKE RECOVERY DATA (cont)			
Compound	Year	Mean ± std dev (%)	(N)
Trichloroethylene	1984	90 ± 8	4
	1985	102 ± 4	3
	1986	106 ± 7	2
	1987	94 ± 6	3
	1988	100 ± 1	4
	1989	90 ± 2	4
Toluene	1984	101 ± 1	3
	1985	105 ± 2	3
	1986	94 ± 6	3
	1987	98 ± 6	8
	1988	86 ± 1	4
	1989	96 ± 3	3
o-Xylene	1984	101 ± 1	3
	1985	103 ± 6	9
	1986	95 ± 5	6
	1987	101 ± 13	7
	1988	89 ± 4	8
	1989	96 ± 4	4

3. Collection and Storage of Samples

3.1. Charcoal tubes are received heat-sealed at both ends with plastic caps to seal the ends after the tubes are opened. OVM badges are received in sealed cans. The OVM badges include a closure cap with center and side ports, a charcoal sorbent disc, and a spacer plate above the disc.

3.2. Spiked tubes and badges are stored in a freezer pending analysis.

4. Apparatus

4.1. Volumetric flasks: 1- and 2-mL, class A, glass.

4.2. Pipettes: Pasteur, disposable, glass.

4.3. Pipette bulb: rubber, to fit Pasteur pipette.

4.4. Syringes: gas-tight, 10-, 25-, 50-, and 100-μL.

4.5. Microspatulas.

4.6. Sorbent sample tubes: charcoal, 100-mg primary bed, 50-mg backup bed.

4.7. Sorbent sample tubes: charcoal, 400-mg primary bed, 200-mg backup bed.

4.8. Organic vapor monitors: 3M OVM #3500 or equivalent from 3M, St. Paul, MN 55144-1000.

4.9. Paper filters: 25 - 28 mm diameter, Whatman #2, #41, #42, or equivalent.

4.10. Teflon tape.

4.11. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.12. Laboratory oven: capable of sustaining 100-150°C.

4.13. Labels printed with QC sample numbers.

5. Reagents

5.1. Carbon disulfide (reagent-grade).

5.2. Methylene chloride (reagent-grade).

5.3. 1,2-Dichloroethane (reagent-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade analytes, chosen primarily from the list of target compounds in Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Add solid analytes first, then liquid analytes after the addition of solvent.

6.2. Solvent choice for the stock solution matrix depends on the analytes included in the solution and on the analytical extraction method. If possible, the solvent should have a shorter chromatographic retention time than the analyte of interest.

6.2.1. Carbon disulfide is the solvent most commonly used.

6.2.2. A stock solution containing carbon disulfide, methylene chloride, or acrylonitrile as an analyte should use 1,2-dichloroethane as a solvent because methylene chloride, acrylonitrile, and carbon disulfide co-elute.

6.2.3. A stock solution containing ethanol as an analyte should use methylene chloride as a solvent because ethanol forms a colloidal suspension in carbon disulfide.

6.2.4. A stock solution containing 1,1,1-trichloroethane as an analyte should use carbon disulfide or methylene chloride as a solvent because 1,1,1-trichloroethane and 1,2-dichloroethane co-elute.

6.3. The stock solution may be prepared in a 1.0- or 2.0-mL volumetric flask. A solution containing multiple analytes is more conveniently prepared in a 2.0-mL volumetric flask.

6.3.1. The usual concentration range of a stock solution is between 5 and 20 mg/mL. A more concentrated stock solution may be required to prepare a QC sample with a higher spike range. The concentration of the stock solution should be such that a spike volume equal to or less than 15 μL onto a small charcoal tube or OVM badge and equal to or less than 30 μL onto a large charcoal tube will bring all analytes into the desired spike range.

6.3.2. Charcoal-tube QC samples prepared to accompany National Institute for Occupational Safety and Health Proficiency Analytical Testing (NIOSH PAT) intercomparison samples are spiked in the range 0.2-2 mg/tube. A stock solution with analytes in the concentration range of 15-150 mg/mL will reach the desired spike range on a small charcoal tube QC sample when a spike volume of 15 μL or less is used.

6.3.3. Add a solid analyte to a clean, tared 1.0- or 2.0-mL volumetric flask to reach the desired stock concentration range. Record the mass of the analyte added and tare the balance. Repeat for each solid analyte. See Step 8.1.

6.3.4. Add the solvent chosen for the stock solution matrix to the volumetric flask until it reaches approximately halfway to the graduation mark. Stopper the flask.

6.3.5. Swirl the flask to dissolve the solid analytes.

6.3.6. Calculate the volumes of the liquid analytes needed to reach the desired stock concentration range. See Steps 8.2 through 8.3.

6.3.7. Place the stoppered flask on the analytical balance and tare the balance.

6.3.8. Add a liquid analyte, from a syringe just above the surface of the solvent, to reach the desired stock concentration range. Restopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte added.

6.3.9. Dilute the solution to volume with the solvent chosen in Step 6.3.4.

6.3.10. Mix by gently inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.3.11. Wrap Teflon tape around the stopper of the volumetric flask.

6.3.12. Label the flask with information identifying the stock solution and with the expiration date.

6.3.13. The stock solution is stable for approximately 2 weeks when stored at -20°C.

6.4. For QC samples containing multiple analytes, more than one stock solution may be prepared using different analytes. The combination of analytes in the QC sample may be varied by spiking with more than one stock solution.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100-150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with semivolatile compounds and a second group of syringes for use only with volatile compounds.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into the waste container. Repeat for a total of 5-10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. The spike range for volatile organic compounds on charcoal tubes or on OVM badges varies with the analyte spiked.

7.3.1. For most analytes, the spike range is 30-100 μg/tube or 30-100 μg/badge.

7.3.2. For analytes with a shorter retention time than carbon disulfide during gas chromatography, the spike range is 100-300 μg/tube or 100-300 μg/badge. Acetone, methanol, ethanol, 2-propanol, and Freon are included in this category.

7.3.3. The spike range for analytes in QC samples prepared to accompany NIOSH PAT samples is 0.2-2 mg/tube.

7.4. Preparation of QC samples for volatile organic compounds on charcoal tubes.

7.4.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.4.2. Use the same size charcoal tube for the QC samples as was used to collect the samples to be analyzed.

7.4.3. The total spike volume onto small charcoal tubes should be equal to or less than 15 μL and onto large charcoal tubes should be equal to or less than 30 μL to avoid saturation of the primary charcoal bed.

7.4.4. Remove the stock solution from the freezer and allow it to come to room temperature. Do not allow the stock solution to sit at room temperature for longer than 1 h before spiking the QC sample.

7.4.5. Break off the tip of the entrance end of the charcoal tube. The entrance end is the end with the glass wool plug over the primary charcoal bed and an air space between the end of the tube and the charcoal bed.

7.4.6. Using a syringe, spike a volume of stock solution onto the primary charcoal bed to reach the desired spike range. Spike the solution beginning in the middle of the primary charcoal bed and drawing the syringe needle toward the glass wool plug at the top of bed as the spiking is completed. The entire volume of spike solution should be on the charcoal bed and not on the walls of the sample tube.

7.4.7. Cap both ends of the sample tube with the plastic tube caps and wrap Teflon tape around the broken end.

7.4.8. Label the tube with a QC sample number.

7.4.9. Return the stock solution to the freezer.

7.4.10. Store the QC samples in a freezer pending analysis.

7.4.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.5. Preparation of QC samples for volatile organic compounds on OVM badges.

7.5.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.5.2. The total spike volume onto an OVM badge should be equal to or less than 15 μL.

7.5.3. Remove the stock solution from the freezer and allow it to come to room temperature. Do not allow the stock solution to sit at room temperature for longer than 1 h before spiking the QC sample.

7.5.4. Remove the OVM badge from the can in which it was received.

7.5.5. Remove and discard the plastic ring and white film from the badge.

7.5.6. Place a 25-28-mm paper filter onto the spacer plate above the charcoal disc. Snap the closure cap onto the badge. Close the side port.

7.5.7. Using a syringe, spike a volume of the stock onto the filter paper through the center port to reach the desired spike range. Close the center port.

7.5.8. Return the badge to the can in which it was received and label the can with a QC number.

7.5.9. The badge should be kept in the refrigerator for at least 16-24 h before analysis to achieve complete transfer of the organic compounds from the filter paper onto the charcoal sorbent or in a freezer for longer periods of time pending analysis.

7.5.10. Return the stock solution to the freezer.

7.5.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Solid analytes used in the stock solution are measured directly by mass.

8.2. Calculate the volume of neat liquid analyte to add to the stock solution as in the following example.

8.2.1. Read the density of the neat liquid analyte from Table I. The density of chloroform is 1.492 mg/μL.

8.2.2. The desired spike range for 1 mL of stock is 5-20 mg of neat analyte.

8.2.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 1 mL of stock solution.

$$\frac{5\ \text{mg}}{1.492\ \text{mg}/\mu\text{L}}\ \text{to}\ \frac{20\ \text{mg}}{1.492\ \text{mg}/\mu\text{L}} = 3.4\ \text{to}\ 13.4\ \mu\text{L}$$

For chloroform, 3.4-13.4 μL of the neat analyte should be diluted to 1 mL to reach the desired concentration range of 5-20 mg/mL in the stock solution.

8.3. Calculate the concentration of each neat analyte in the stock solution as in the following example.

8.3.1. If 5 μL of chloroform, weighing 7.5 mg, is diluted to 1 mL of stock solution, the concentration of chloroform in the stock solution is 7.5 mg/mL.

$$\frac{7.5\ \text{mg}}{1\ \text{mL}} = 7.5\ \text{mg/mL}$$

8.4. Calculate the concentration of each analyte on a charcoal tube QC sample as in the following example.

8.4.1. If 6 μL of a stock solution containing 7.5 mg/mL of chloroform is spiked onto a charcoal tube, the concentration of chloroform in the QC sample is 45 μg/sample. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(7.5\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(6\ \mu\text{L})}{\text{sample}} = 45\ \mu\text{g/sample}$$

8.5. Calculate the concentration of each analyte on an OVM badge QC sample as in the following example.

8.5.1. If 9 μL of a stock solution containing 7.5 mg/mL of chloroform is spiked onto an OVM badge, the concentration of chloroform in the QC sample is 67.5 μg/sample. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(7.5\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(9\ \mu\text{L})}{\text{sample}} = 67.5\ \mu\text{g/sample}$$

8.6. Record the analyte concentration on a charcoal tube QC sample or an OVM badge as μg/sample or mg/sample.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep in the sealed container pending pickup by Waste Management (CST-7).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full, and keep the can in the secondary containment tray pending pickup by CST-7.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full, and keep the jar in the secondary containment tray pending pickup by CST-7.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up a full bag, can, or jar of waste contaminated with organic compounds using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

10.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

10.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

10.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

10.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

10.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.7. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

TABLE I. ORGANIC COMPOUNDS

Compound	CAS Number	Density of liquids (mg/μL)
acetone	67641	0.791
benzene	71432	0.874
bromobenzene	108861	1.491
bromochloromethane	74975	1.991
bromodichloromethane	75274	1.980
bromoform	75252	2.894
bromomethane	74839	0.838
2-butanone (MEK)	78933	0.805
n-butylbenzene	104518	0.860
sec-butylbenzene	135988	0.863
tert-butylbenzene	98066	0.867
carbon disulfide	75150	1.266
carbon tetrachloride	56235	1.594
chlorobenzene	108907	1.107
chlorodibromomethane	124481	2.451
chloroethane	75003	0.891
chloroform	67663	1.492
1-chlorohexane	544105	0.879
2-chlorotoluene	95498	1.083
4-chlorotoluene	106434	1.070
1,2-dibromo-3-chloropropane	96128	2.093
1,2-dibromoethane	106934	2.180
dibromomethane	74953	2.477
1,2-dichlorobenzene	95501	1.306
1,3-dichlorobenzene	541731	1.288
1,4-dichlorobenzene	106467	1.241
1,1-dichloroethane	75343	1.176
1,2-dichloroethane	107062	1.256
1,1-dichloroethene	75354	1.213
cis-1,2-dichloroethene	156592	1.284
trans-1,2-dichloroethene	156605	1.257
1,2-dichloropropane	78875	1.156
1,3-dichloropropane	142289	1.190
2,2-dichloropropane	594207	1.082
1,1-dichloropropene	563586	1.169
cis-1,3-dichloropropene	10061015	1.224
trans-1,3-dichloropropene	10061026	1.224
ethylbenzene	100414	0.867
hexachlorobutadiene	87683	1.665

TABLE I. ORGANIC COMPOUNDS (cont)

Compound	CAS Number	Density of liquids (mg/μL)
2-hexanone	591786	0.812
isopropylbenzene	98828	0.864
4-isopropyltoluene	99876	0.860
methylene chloride	75092	1.325
4-methyl-2-pentanone (MIK)	108101	0.800
naphthalene	91203	solid
n-propylbenzene	103651	0.862
styrene	100425	0.909
1,1,1,2-tetrachloroethane	630206	1.598
1,1,2,2,-tetrachloroethane	79345	1.586
tetrachloroethene	127184	1.623
toluene	108883	0.867
1,2,3-trichlorobenzene	87616	solid
1,2,4-trichlorobenzene	120821	1.454
1,1,1-trichloroethane	71556	1.338
1,1,2-trichloroethane	79005	1.435
trichloroethene	79016	1.464
trichlorofluoromethane	75694	1.494
1,2,3-trichloropropane	96184	1.387
1,2,4-trimethylbenzene	95636	0.889
1,3,5-trimethylbenzene	108678	0.864
vinyl acetate	108054	0.934
o-xylene	95476	0.870
mixed xylenes (total)	1330207	0.860

PESTICIDES ON SOIL — QC SAMPLE PREPARATION

Analyte: Pesticides	**Method No.:** QCO140
Matrix: Soil	**Spike Range:** 10–150 μg/kg
Procedure: Analysis by solvent extraction followed by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** 100% ± 4.4% RSD
Effective Date: 01/22/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in acetone of one to six individual pesticides, selected primarily from the list in Sec. 6, Table II.

1.2. Prepare a 1:100 dilution in methanol of the stock solution.

1.3. Spike the 1:100 dilution directly onto blank soil.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, volumetric flask, and balance. A relative standard deviation (RSD) of 4.4% at the 1-σ level has been calculated for the error of the standard and for the spiking and weighing process based on the following function:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7} ,$$

where D = calculated result,
M1 = standard error,
M2 = first weighing error,
M3 = first dilution error,
M4 = first spiking error,

M5 = second dilution error,
M6 = second spiking error, and
M7 = second weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6} + R^2_{M7}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of first balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of second balance, and
100 = factor to convert to percentage.

2.2. Analysis by solvent extraction and gas chromatography of QC samples prepared using this procedure from 1990 to 1992 are summarized in Table I below. The data are published in Source Materials 10.1 through 10.3.

TABLE I. PESTICIDES-ON-SOIL SPIKE RECOVERY DATA		
Compound	% Recovery Mean ± std dev	(N)
Lindane	71 ± 25	(6)
α-BHC	69 ± 18	(5)
Aldrin	—	
β-BHC	75 ± 18	(2)
δ-BHC	—	
Dieldrin	—	
Endosulfan I	—	
Endosulfan II	—	
Endrin	78 ± 22	(8)
Heptachlor epoxide	74 ± 16	(5)
p,p´-DDD	63 ± 24	(7)
p,p´-DDE	78 ± 15	(3)
p,p´-DDT	70 ± 36	(8)
Methoxychlor	63 ± 15	(6)
Endosulfan sulfate	—	

3. Collection and Storage of Samples

3.1. The blank soil matrix and the spiked samples should be stored in glass bottles fitted with Teflon-lined lids. Avoid using plastic containers and lids because phthalates, which are semivolatile compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for the extraction of pesticides on soil is 14 days.

4. Apparatus

4.1. Volumetric flasks: 10- and 25-mL, class A, glass.

4.2. Syringes: gas-tight, 25-, 50-, 100-, and 500-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Bulbs: rubber, to fit Pasteur pipettes.

4.6. Bottles: 2-oz, amber, glass, with Teflon-lined caps.

4.7. Teflon tape.

4.8. Bottles: 2-oz, glass, with Teflon-lined caps.

4.9. Analytical balance: 200-g minimum capacity, 0.1-mg accuracy.

4.10. Drying oven: capable of sustaining 100–150°C.

4.11. Labels: printed with QC sample numbers.

5. Reagents

5.1. Soil: a clean, dry 30-g aliquot is required for each sample.

5.2. A suitable soil does not contain the analyte of interest and presents few interferences to the analytical method.

5.3. Blank soil heated to nominally 100°C for 5 h and stored in glass is used as a sample matrix.

5.4. Acetone (analytical-grade).

5.5. Methanol (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade pesticides selected primarily from the list in Table II. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19387).

6.1.1. Determine the desired concentration of each analyte included in the stock solution. Typical ranges for the concentrated stock solution are listed in Table II. The concentration of an analyte in the stock solution may be varied depending on the desired spike range for the analyte in the QC sample.

TABLE II. TYPICAL CONCENTRATON RANGES FOR QC SAMPLES AND CONCENTRATED STOCK SOLUTIONS FOR VARIOUS PESTICIDES

Compound	CAS numbers	QC Samples µg/kg	Concentrated stock mg/mL
Lindane	58899	10–20	1–2
α-BHC	319846	10–20	1–2
Aldrin	309002	20–40	2–4
β-BHC	319857	20–40	2–4
δ-BHC	319868	20–40	2–4
Dieldrin	60571	20–40	2–4
Endosulfan I	959988	20–40	2–4
Endosulfan II	33213659	20–40	2–4
Endrin	72208	20–40	2–4
Heptachlor epoxide	1024573	20–40	2–4
p,p′-DDD	72548	20–40	2–4
p,p′-DDE	72559	20–40	2–4
p,p′-DDT	50293	20–40	2–4
Methoxychlor	72435	50–150	5–15
Endosulfan sulfate	1031078	50–150	5–15

6.1.2. Add the desired amount of a solid pesticide analyte to a clean, tared 10.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.3. Add approximately 7 mL of acetone to the flask and swirl to dissolve the analytes.

6.1.4. Dilute the solution to volume with acetone.

6.1.5. Mix by inversion.

6.1.6. Transfer the stock solution to a 2-oz amber bottle with a Teflon-lined lid. Cap the bottle.

6.1.7. Label the bottle with information identifying the standard.

6.1.8. Weigh the capped and labeled bottle containing the standard and record the mass and date on the label.

6.1.9. Wrap Teflon tape around the cap.

6.1.10. The stock solution is stable for at least 3 months stored at room temperature. Refrigeration may cause some of the analytes to precipitate.

6.1.11. Before each use, remove the Teflon tape from the bottle, weigh the bottle, and compare the mass to the most recent mass recorded on the bottle label. Any significant loss in mass is attributed to evaporation of the acetone matrix. Make up the loss by adding enough acetone to reach the most recent mass recorded on the label, restoring the stock solution to its original concentration.

6.2. Prepare a 1:100 dilution of the stock solution.

6.2.1. Remove the Teflon tape from the bottle of pesticide stock solution, weigh the bottle, and, if necessary, adjust the concentration of the stock by adding acetone as described in Step 6.1.11.

6.2.2. Add approximately 20 mL of methanol to a clean 25-mL volumetric flask.

6.2.3. Using a gas-tight syringe, add 250 μL of the pesticide stock solution just above the surface of the methanol.

6.2.4. Cap the bottle of pesticide stock solution and weigh the capped bottle.

6.2.5. Record the date and the mass of the capped bottle of solution on the bottle label and cross out the previous date and mass.

6.2.6. Wrap Teflon tape around the bottle cap.

6.2.7. Dilute the solution in the 25-mL volumetric flask to volume with methanol.

6.2.8. Mix by inversion.

6.2.9. Transfer the 1:100 dilution to a 2-oz amber bottle with a Teflon-lined lid. Cap the bottle.

6.2.10. Label the bottle with information identifying the dilution.

6.2.11. Weigh the capped and labeled bottle containing the dilution and record the mass and date on the label.

6.2.12. Wrap Teflon tape around the cap.

6.2.13. The diluted stock solution is stable for at least 3 months stored at room temperature. Refrigeration may cause some of the analytes to precipitate.

6.2.14. Before each use, remove the Teflon tape from the bottle, weigh the bottle, and compare the mass to the most recent mass recorded on the bottle label. Any significant loss in mass is attributed to evaporation of the methanol matrix. Make up the loss by adding enough methanol to reach the most recent mass recorded on the label, restoring the dilution to its original concentration.

7. Procedure

7.1. Cleaning of glassware.

7.1.1. Wash volumetric flasks with detergent and rinse them with hot tap water and methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use with pesticide analytes.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for a minimum of 10 min.

7.3. Preparation of QC samples.

7.3.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.2. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a pesticides-on-soil QC sample using 30 g of blank soil and a 2-oz glass bottle.

7.3.3. Accurately weigh 30 g of blank soil into a 2-oz glass bottle with a Teflon-lined lid. Record the mass of soil on the bottle with a felt-tipped pen for reference by the analyst.

7.3.4. Remove the Teflon tape from the bottle containing the 1:100 dilution of the pesticide stock.

7.3.5. Weigh the bottle and compare the mass to the most recent mass recorded on the label.

7.3.6. If a significant loss in mass has occurred due to evaporation of the methanol matrix, add enough methanol to the dilution to reach the most recent mass recorded on the label, restoring the solution to its original concentration as described in Step 6.2.14.

7.3.7. If methanol has been added, mix the solution by swirling the bottle.

7.3.8. Using a gas-tight syringe, spike a volume of the 1:100 dilution onto the surface of the soil to reach the desired spike range. Cap the bottle containing the dilution. Blank samples may be made by spiking methanol onto the soil. The analyst will use the entire sample.

7.3.9. Cap the vial containing the spiked soil sample and label it with a QC number.

7.3.10. Refrigerate the sample pending analysis. The maximum holding time for a pesticides-on-soil QC sample is 14 days.

7.3.11. Weigh the capped bottle containing the 1:100 stock dilution. Record the date and the new mass on the label on the bottle and cross out the previous date and mass.

7.3.12. Wrap Teflon tape around the cap and store the solution at room temperature.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of each analyte in the stock solution as in the following example.

8.1.1. If 18.0 mg of Lindane is dissolved in 10.0 mL of acetone, the concentration of Lindane in the stock solution is 1.8 mg/mL.

$$\frac{18.0 \text{ mg}}{10.0 \text{ mL}} = 1.8 \text{ mg/mL} .$$

8.2. Calculate the concentration of each analyte in the 1:100 dilution of the stock solution as in the following example.

8.2.1. If 250 μL of a stock solution containing 1.8 mg/mL of Lindane is diluted to 25 mL with methanol, the concentration of Lindane in the 1:1000 dilution is 18 μg/mL.

$$\frac{\left(\frac{1.8\ \text{mg}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(250\ \mu\text{L})\left(\frac{1000\mu\text{g}}{1\ \text{mg}}\right)}{25\ \text{mL}} = 18\ \mu\text{g/mL}\ .$$

8.3. Calculate the concentration of each analyte in the QC sample as in the following example.

8.3.1. If 25 μL of a 1:100 stock dilution containing 18 μg/mL Lindane is spiked onto 30.0000 g of blank soil, the concentration of Lindane in the QC sample is 15 μg/kg.

$$\frac{\left(\frac{18\mu\text{g}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\mu\text{L}}\right)(25\ \mu\text{L})}{30.0000\ \text{g}\ \left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)} = 15\ \mu\text{g/kg}\ .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record analyte concentrations in the QC sample in μg/kg or μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) contaminated with organic compounds in a covered metal can lined with a plastic bag and keep it segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the sealed bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) in a covered metal can in a secondary containment tray.

9.2.1.1. Keep liquid waste containing organic compounds segregated from PCB-contaminated liquid waste and from waste that does not contain organic compounds.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Open the can only for the period of time necessary to add waste.

9.2.1.4. When the can is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.5. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB contaminated.

9.2.2.2. Label the bottle with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the bottle only for the time necessary to add vials.

9.2.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new bottle for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full container of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

PESTICIDES IN WATER — QC SAMPLE PREPARATION

Analyte: Pesticides	**Method No.:** QCO150
Matrix: Water	**Spike Range:** 0.1–1.5 μg/L
Procedure: Analysis by solid phase extraction followed by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** 100% ± 4.4% RSD
Effective Date: 03/01/90	**Author:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in acetone of one to six individual pesticides selected primarily from the list in Sec. 6, Table I.

1.2. Prepare a 1:1000 dilution in methanol of the stock solution.

1.3. Spike the 1:1000 dilution directly into distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. Since the analyst uses the entire sample, it is not necessary to dilute the sample to exactly 1L, and the assumption is made that M7=1. A relative standard deviation (RSD) of 4.4% at the 1-σ level has been calculated for standard preparation and for the weighing, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7},$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,

M3 = first dilution error,
M4 = first pipette error,
M5 = second dilution error,
M6 = second pipette error, and
M7 = third dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation. Since the analyst uses the entire sample, it is not necessary to dilute the sample to exactly 1L, and the assumption is made that $R^2_{M7}=0$.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6} + R^2_{M7}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of third volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by solid phase extraction and gas chromatography of QC samples (N = 3) prepared using this procedure from 1990 through 1992 gave a mean recovery of 68% ± 21% at the 1-σ level. The data are published in Source Materials 10.1 through 10.3.

3. Collection and Storage of Samples

3.1. Distilled water is used as the blank matrix for spiking. Use water that has not been run through plastic tubing or stored in plastic holding vessels because phthalates, which are semivolatile organic compounds, may leach from plastics and contaminate the samples.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for pesticides in water is 7 days.

4. Apparatus

4.1. Volumetric flasks: 10- and 50-mL, class A, glass.

4.2. Syringes: gas-tight, 25-, 50-, 100-, 250-, and 500-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Bulbs: rubber, to fit Pasteur pipettes.

4.6. Bottles: 2-oz , amber, glass, with Teflon-lined caps.

4.7. Teflon tape.

4.8. Bottles: 1-L, wide-mouth, amber glass, precleaned, with Teflon-lined lids.

4.9. Analytical balance: 200-g minimum capacity, 0.1-mg accuracy.

4.10. Drying oven: capable of sustaining 100–150°C.

4.11. Labels: printed with QC sample numbers.

5. Reagents

5.1. Acetone (analytical-grade).

5.2. Methanol (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade pesticides selected primarily from the list in Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19387).

6.1.1. Determine the desired concentration of each analyte in the stock solution. Typical ranges for the concentrated stock solution are listed in Table I. The concentration of an analyte in the stock solution may be varied depending on the desired spike range for the analyte in the QC sample.

TABLE I. TYPICAL CONCENTRATION RANGES FOR QC SAMPLES AND CONCENTRATED STOCK SOLUTIONS FOR VARIOUS PESTICIDES

Compounds	CAS numbers	QC samples µg/L	Concentrated stock mg/mL
Lindane	58899	0.1–0.2	1–2
α-BHC	319846	0.1–0.2	1–2
Aldrin	309002	0.2–0.4	2–4
β-BHC	319857	0.2–0.4	2–4
δ-BHC	319868	0.2–0.4	2–4
Dieldrin	60571	0.2–0.4	2–4
Endosulfan I	959988	0.2–0.4	2–4
Endosulfan II	33213659	0.2–0.4	2–4
Endrin	72208	0.2–0.4	2–4
Heptachlor epoxide	1024573	0.2–0.4	2–4
p,p′-DDD	72548	0.2–0.4	2–4
p,p′-DDE	72559	0.2–0.4	2–4
p,p′-DDT	50293	0.2–0.4	2–4
Methoxychlor	72435	0.5–1.5	5–15
Endosulfan sulfate	1031078	0.5–1.5	5–15

6.1.2. Add the desired amount of a solid pesticide analyte to a clean, tared 10.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.3. Add approximately 7 mL of acetone to the flask and swirl it to dissolve all the analytes.

6.1.4. Dilute the solution to volume with acetone.

6.1.5. Mix by inversion.

6.1.6. Transfer the stock to a 2-oz amber bottle with a Teflon-lined lid. Cap the bottle.

6.1.7. Label the bottle with information identifying the standard.

6.1.8. Weigh the capped and labeled bottle containing the standard and record the mass and date on the label.

6.1.9. Wrap Teflon tape around the cap.

6.1.10. The stock solution is stable for at least 3 months stored at room temperature. Refrigeration may cause some of the analytes to precipitate.

6.1.11. Before each use, remove the Teflon tape from the bottle, weigh the bottle, and compare the mass to the most recent mass recorded on the bottle label. Any significant loss in mass is attributed to evaporation of the acetone matrix. Make up the loss by adding enough acetone to reach the most recent mass recorded on the label, restoring the stock solution to its original concentration.

6.2. Prepare a 1:1000 dilution of the stock solution.

6.2.1. Remove the Teflon tape from the bottle of pesticide stock solution, weigh the bottle, and, if necessary, adjust the concentration of the stock by adding acetone as described in Step 6.1.11.

6.2.2. Add approximately 40 mL of methanol to a clean 50-mL volumetric flask.

6.2.3. Using a gas-tight syringe, add 50 μL of the pesticide stock solution just above the surface of the methanol.

6.2.4. Cap the bottle of pesticide stock solution and weigh the capped bottle.

6.2.5. Record the date and the mass of the capped bottle of solution on the bottle label and cross out the previous date and mass.

6.2.6. Wrap Teflon tape around the bottle cap.

6.2.7. Dilute the solution in the 50-mL volumetric flask to volume with methanol.

6.2.8. Mix by inversion.

6.2.9. Transfer the 1:1000 dilution to a 2-oz amber bottle with a Teflon-lined lid. Cap the bottle.

6.2.10. Label the bottle with information identifying the dilution.

6.2.11. Weigh the capped and labeled bottle containing the dilution and record the mass and date on the label.

6.2.12. Wrap Teflon tape around the cap.

6.2.13. The diluted stock solution is stable for at least 3 months stored at room temperature. Refrigeration may cause some of the analytes to precipitate.

6.2.14. Before each use, remove the Teflon tape from the bottle, weigh the bottle, and compare the mass to the most recent mass recorded on the bottle label. Any significant loss in mass is attributed to evaporation of the methanol matrix. Make up the loss by adding enough methanol to reach the most recent mass recorded on the label, restoring the dilution to its original concentration.

7. Procedure

7.1. Cleaning of glassware.

7.1.1. Wash volumetric flasks with detergent and rinse them with hot tap water and methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100–150°C to minimize contamination.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use with pesticide analytes.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for a minimum of 10 min.

7.3. Preparation of QC samples.

7.3.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.2. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a 1-L pesticides-in-water QC sample in an amber glass jar.

7.3.3. Remove the Teflon tape from the bottle containing the 1:1000 dilution of the pesticide stock.

7.3.4. Weigh the dilution and compare the mass to the most recent mass recorded on the bottle label.

7.3.5. If a significant loss in mass has occurred due to evaporation of the methanol matrix, add enough methanol to the dilution to reach the most recent mass recorded on the label, restoring the dilution to its original concentration as described in Step 6.2.14.

7.3.6. If methanol has been added, mix the solution by swirling the bottle.

7.3.7. Fill a precleaned 1-L amber bottle to the neck with distilled water. Use only distilled water that has not been stored in plastic or run through plastic tubing.

7.3.8. Using a gas-tight syringe, spike a volume of the 1:1000 dilution beneath the surface of the water to reach the desired spike range. Cap the bottle containing the dilution. Blank QC samples may be made by spiking methanol instead of stock dilution.

7.3.9. Cap the bottle containing the QC sample and label it with a QC sample number.

7.3.10. The analyst will use the entire sample assuming a 1-L volume.

7.3.11. Refrigerate the sample pending analysis. The maximum holding time for a pesticides-in-water QC sample is 7 days.

7.3.12. Weigh the capped bottle containing the 1:1000 stock dilution. Record the date and the new mass on the label on the bottle and cross out the previous date and mass.

7.3.13. Wrap Teflon tape around the cap and store the dilution at room temperature.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of each analyte in the stock solution as in the following example.

8.1.1. If 18.0 mg of Lindane is dissolved in 10.0 mL of acetone, the concentration of Lindane in the stock solution is 1.8 mg/mL.

$$\frac{18.0\ \text{mg}}{10.0\ \text{mL}} = 1.8\ \text{mg/mL}\ .$$

8.2. Calculate the concentration of each analyte in the 1:1000 dilution of the stock solution as in the following example.

8.2.1. If 50 μL of a stock solution containing 1.8 mg/mL of Lindane is diluted to 50 mL with methanol, the concentration of Lindane in the 1:1000 dilution is 1.8 μg/mL.

$$\frac{\left(\frac{1.8\ \text{mg}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(50\ \mu\text{L})\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{50\ \text{mL}} = 1.8\ \mu\text{g/mL}\ .$$

8.3. Calculate the concentration of each analyte in the QC sample as in the following example.

8.3.1. If 80 μL of a 1:1000 stock dilution containing 1.8 μg/mL of Lindane is spiked into 1 L of distilled water, the concentration of Lindane in the QC sample is 0.14 μg/L.

$$\frac{\left(\frac{1.8\ \mu\text{g}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(80\ \mu\text{L})}{(1\ \text{L})} = 0.14\ \mu\text{g/L}\ .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record analyte concentrations in the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) contaminated with organic compounds in a covered metal can lined with a plastic bag and

keep it segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the sealed bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Accumulate liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) in a covered metal can in a secondary containment tray.

9.2.1.1. Keep liquid waste containing organic compounds segregated from PCB-contaminated liquid waste and from waste that does not contain organic compounds.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the can is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.1.5. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB contaminated.

9.2.2.2. Label the bottle with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the bottle only for the time necessary to add vials.

9.2.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new bottle for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full container of waste contaminated with organic compounds by using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. The CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

POLYCHLORINATED BIPHENYLS IN OIL — QC SAMPLE PREPARATION

Analyte: Polychlorinated biphenyls (PCBs)	**Method No.:** QCO170
Matrix: Oil	**Spike Range:** 10–500 μg/g oil
Procedure: Analysis by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** EPA standards - 100% ± 10.0% RSD CST-3 standards - 100% ± 1.5% RSD
Effective Date: 09/15/86	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 to 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions of Aroclor 1242, 1254, and 1260 in hexane or obtain Environmental Protection Agency (EPA) Aroclor 1242, 1254, and 1260 standards. Refer to the table below for Aroclors and associated Chemical Abstract Service (CAS) numbers.

Compound	CAS Number
Aroclor 1242	53469219
Aroclor 1254	11097691
Aroclor 1260	11096825
Total PCBs	1336363

1.2. Spike the stock solution into a blank oil sample.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with the use of the microsyringe and of the balance. A relative standard deviation (RSD) of 10% for EPA standards and 1.5% for in-house standards has been calculated for the error of the standard and for spiking and weighing based on the following:

2.1.1. EPA standard.

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = standard error,
M2 = spiking error, and
M3 = weighing error.

2.1.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of microsyringe,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.1.2. In-house standard.

$$U = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where U = uncertainty,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = second weighing error, and
M5 = spiking error.

2.1.2.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable.

2.1.2.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2 + R_{M5}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of second balance,
R^2_{M5} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1990 and 1992 using this procedure and analyzed by GCECD are summarized in Table I. The data are published in Source Materials 10.1 through 10.3.

TABLE I. PCB-IN-OIL SPIKE RECOVERY DATA (% recovery ±std dev)

	1990 Mean ± std dev	N	1991 Mean ± std dev	N	1992 Mean ± std dev	N
Aroclor 1242	96 ± 19	(56)	112 ± 20	(49)	121 ± 38	(60)
Aroclor 1254	—				103 ± 43	(10)
Aroclor 1260	79 ± 14	(88)	96 ± 23	(78)	87 ± 31	(80)
Total Aroclor	86 ± 18	(143)	102 ± 127	(127)	102 ± 38	(150)

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis. Samples prepared in 1986 and analyzed through 1991 have shown no decrease in analyte recovery.

4. Apparatus

4.1. Volumetric flasks: 5-mL, class A, glass.

4.2. Gas-tight syringes: 50-, 250-, 500-, and 2500-μL.

4.3. Bottles: 2- and 8-oz, glass, with Teflon-lined lids.

4.4. Vials: 1.5-mL glass.

4.5. Caps: open-top to fit 1.5-mL vials.

4.6. Septa: Teflon/silicone discs to fit open-top caps.

4.7. Teflon tape.

4.8. Pipettes: Pasteur, disposable glass.

4.9. Pipette bulb: rubber, to fit Pasteur pipette.

4.10. Stirring rod: glass, 3- to 4-mm-diam.

4.11. Autosampler vials with Teflon-lined septa and crimp tops: 11- x 30-mm vials, and 11-mm silicone liner with Teflon face.

4.12. Portable crimper for sealing caps on autosampler vials.

4.13. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.14. Analytical balance: 400-g minimum capacity, 1-mg accuracy.

4.15. Ultrasonic mixer.

4.16. Labels printed with QC sample numbers.

5. Reagents

5.1. Hexane (analytical-grade).

5.2. Blank vacuum pump oil. Any oil selected should be checked for interferences with the specific Aroclor chromatographic patterns.

6. Calibration and Standards

6.1. EPA Aroclor standards in isooctane or methanol are available in concentrations between 500 and 3000 μg/mL.

6.2. After opening the heat-sealed ampule containing an Aroclor standard, transfer the contents into a vial with a screw cap with Teflon/silicone septum. Wrap the cap with Teflon tape. Remove the original label and affix it to the vial or transfer the standards information to a label on the vial.

6.3. Solutions of PCBs may be prepared from pure PCBs in concentrations of 50–60 mg/mL.

6.4. Preparation of in-house standards in hexane.

6.4.1. Tare a 5-mL volumetric flask on a balance accurate to 0.1 mg. Add approximately 250–300 mg of a pure PCB to the bottom of the flask using a glass Pasteur pipette or a glass stirring rod. Record the mass added.

6.4.2. Dissolve the PCB and dilute it to volume with hexane. Mix by inversion.

6.4.3. Prepare a separate standard solution for each PCB desired. Do not mix Aroclors.

6.4.4. The standard concentration will be 50–60 mg/mL. See Step 8.1.

6.4.5. Transfer the standard to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.4.6. Label the vials with information identifying the standard.

6.5. Store the stock standards in a freezer.

7. Procedure

7.1. Discard used, PCB-contaminated flasks, bottles, and pipettes in the PCB waste container.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use only with PCBs.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. QC samples may be prepared in larger or smaller quantities than described in this procedure, adjusting apparatus size as necessary. Preparation of 200 g of a PCB-in-oil QC sample from an in-house standard or of 10 g of a PCB-in-oil QC sample from an EPA standard is described in this procedure.

7.4. QC sample preparation using in-house Aroclor standards.

7.4.1. Remove a vial of the desired in-house Aroclor standard from the freezer and allow it to reach room temperature.

7.4.2. Tare a clean 8-oz glass bottle on a balance accurate to 1 mg or better.

7.4.3. Add approximately 200 g of blank vacuum pump oil to the bottle. Record the mass of oil added.

7.4.4. Spike an aliquot of an in-house Aroclor standard into the oil using a syringe to reach the desired spike range. See Step 8.2.

7.4.5. Cap the bottle with a Teflon lid and label it with information identifying the sample.

7.4.6. Return the vial containing the in-house Aroclor standard to the freezer.

7.4.7. Prepare several PCB-in-oil QC samples using different Aroclors in hexane and different spike volumes to cover the entire spike range.

7.4.8. Mix the PCB-in-oil QC samples for at least 8 h in an ultrasonic mixer.

7.4.9. Store the samples at room temperature.

7.5. QC sample preparation using EPA Aroclor standards.

7.5.1. Choose an EPA Aroclor standard with a concentration between 500 and 3000 μg/mL to reach the desired concentration range in 10 g of oil.

7.5.2. Remove a vial of the chosen Aroclor standard from the freezer and allow it to reach room temperature.

7.5.3. Tare a clean 2-oz glass bottle on a balance accurate to 1 mg or better.

7.5.4. Add approximately 10 g of blank vacuum pump oil to the bottle. Record the mass of oil added.

7.5.5. Using a syringe, spike an aliquot of EPA aroclor standard into the oil to reach the desired spike range. See Step 8.3.

7.5.6. Cap the bottle with a Teflon lid and label it with information identifying the sample.

7.5.7. Return the vial containing the Aroclor standard to the freezer.

7.5.8. Prepare several PCB-in-oil QC samples using different EPA Aroclors and different spike volumes to cover the entire spike range.

7.5.9. Mix the PCB-in-oil QC samples for at least 8 h in an ultrasonic mixer.

7.5.10. Store the samples at room temperature.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.7. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.7.1. Aliquot 1–2 mL of a PCB-in-oil QC sample into an autosampler vial and seal the vial with a crimp-top cap.

7.7.2. Label the vial with a QC sample number.

8. Calculations

8.1. Calculate the concentration of the in-house Aroclor standard prepared from pure PCBs as in the following example.

8.1.1. If 275.0 mg of pure PCB is diluted to 5.0 mL with hexane, the concentration of the PCB in the standard is 55 mg/mL.

$$\frac{275.0 \text{ mg}}{5.0 \text{ mL}} = 55 \text{ mg/mL} \quad .$$

8.2. Calculate spike concentrations from an in-house Aroclor standard as in the following example.

8.2.1. If 150 μL of a 55-mg/mL in-house Aroclor standard is spiked into 198.0 g of blank oil, the PCB concentration in the QC sample is 42 μg/g.

$$\frac{(55\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(150\ \mu\text{L})}{198.0\ \text{g}} = 42\ \mu\text{g/g} \quad .$$

8.2.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.3. Calculate spike concentrations from an EPA Aroclor standard as in the following example.

8.3.1. If 800 μL of a 3000-μg/mL EPA Aroclor standard is spiked into 10 g of blank oil, the PCB concentration in the QC sample is 240 μg/g.

$$\frac{(3000\ \mu\text{g/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(800\ \mu\text{L})}{10\ \text{g}} = 240\ \mu\text{g/g} \quad .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record the Aroclor concentrations in the QC samples in μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. PCB-contaminated solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) is accumulated in a covered metal can lined with a plastic bag and is kept segregated from non-PCB-contaminated solid waste.

9.1.2. The can is labeled with a label indicating its use for PCB-contaminated waste.

9.1.3. The can is opened only for the time necessary to add waste.

9.1.4. When the plastic bag is full, it is sealed with tape, removed from the can, identified as PCB-contaminated waste, and placed in a functioning chemical exhaust hood pending pickup by Waste Services (CST-17).

9.1.5. A new plastic bag is put into the waste can for continued use.

9.2. Liquid waste.

9.2.1. PCB-contaminated liquid waste (such as rinses from PCB-contaminated syringes, PCB standards, and incorrectly spiked QC samples) is accumulated in a covered polyethylene bottle in a secondary containment tray and is kept segregated from non-PCB-contaminated liquid waste.

9.2.2. The bottle is labeled with a label indicating its use for PCB-contaminated waste and with a hazardous waste label if the waste contains hazardous components.

9.2.3. The bottle is opened only for the time necessary to add waste.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag or bottle of PCB-contaminated waste by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994) .

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Polychlorinated Biphenyls," Administrative Requirement 10-4, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

POLYCHLORINATED BIPHENYLS IN WATER — QC SAMPLE PREPARATION

Analyte: Polychlorinated biphenyls (PCBs)	**Method No.:** QCO180
Matrix: Water	**Spike Range:** 1–25 μg/L
Procedure: Analysis by gas chromatography with electron capture detection	**Accuracy and Precision:** 100% ± 4.3%
Effective Date: 01/23/92	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.2 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions of Aroclor 1242, 1254, and 1260 in methanol using pure Aroclor standards. Refer to the table below for Aroclors and associated Chemical Abstract Service (CAS) numbers.

Compound	CAS Number
Aroclor 1242	53469219
Aroclor 1254	11097691
Aroclor 1260	11096825
Total PCBs	1336363

1.2. Prepare a dilution of the PCB stock solutions.

1.3. Spike the dilution of the stock solution into 500 mL of distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with the use of the microsyringe, balance, and volumetric flask. Since the analyst uses the entire sample, it is not necessary to dilute the sample to exactly 500 mL, and the assumption is made that M7 = 1. A relative standard deviation (RSD) of 4.3% at the 1-σ level has

been calculated for standard preparation and for the weighing, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = first dilution error,
M4 = first pipette error,
M5 = second dilution error,
M6 = second pipette error, and
M7 = third dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation. Since the analyst uses the entire sample, it is not necessary to dilute the sample to exactly 500 mL, and the assumption is made that $R^2_{M7} = 0$.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6} + R^2_{M7}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,

R^2_{M7} = relative variance of third volumetric flask, and
100 = factor to convert to percentage.

3. Collection and Storage of Samples

3.1. Distilled water is used as the blank matrix. Use water that has not been run through plastic tubing or stored in plastic holding vessels because phthalates, which are semivolatile organic compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. There is no holding time requirement for the analysis of PCB-in-water samples.

4. Apparatus

4.1. Volumetric flasks: 5- and 10-mL, class A, glass.

4.2. Stirring rod: glass, 3- to 4-mm diam.

4.3. Pipettes: Pasteur, disposable glass.

4.4. Bulbs: rubber, to fit Pasteur pipettes.

4.5. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.6. Vials: 1.5-mL, glass.

4.7. Caps: open-top to fit 1.5-mL vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Syringes: gas-tight, 25-, 50-, 100-, 250-, and 500-μL.

4.11. Bottles: 500-mL, wide-mouth, glass, amber, precleaned, with Teflon-lined lids.

4.12. Drying oven: capable of sustaining 100–150°C.

4.13. Labels printed with QC sample numbers.

5. Reagents

5.1. Methanol (analytical-grade).

6. Calibration and Standards

6.1. Prepare standard solutions from pure Aroclors in concentrations of 1–2 mg/mL.

6.1.1. Tare a 10-mL volumetric flask on an analytical balance.

6.1.2. Add approximately 10–20 mg of a pure Aroclor to the flask using a glass Pasteur pipette or a glass stirring rod. Record the mass added.

6.1.3. Dissolve the Aroclor and dilute it to volume with methanol. Mix by inversion.

6.1.4. Prepare a separate standard solution for each Aroclor desired. Do not mix Aroclors.

6.1.5. The concentration of PCB in the standard will be 1–2 mg/mL. See Step 8.1.

6.1.6. Transfer the standard to 1.5-mL vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.7. Label the vials with information identifying the standard.

6.2. Prepare a dilution in methanol of the Aroclor standard solution at a concentration of approximately 50 μg/mL.

6.2.1. Add 4 mL of methanol to a clean 5-mL volumetric flask.

6.2.2. Using a syringe, add an aliquot of the Aroclor standard with a concentration of 1–2 mg/mL to reach a PCB concentration in the dilution of approximately 50 μg/mL.

6.2.3. Bring the dilution to volume with methanol. Mix by inversion.

6.2.4. The concentration of PCB in the dilution should be approximately 50 μg/mL. See Step 8.2.

6.2.5. Transfer the dilution to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the cap.

6.2.6. Label the vials with information identifying the standard.

6.3. Store the standard solutions and dilutions in a freezer.

7. Procedure

7.1. Discard used, PCB-contaminated flasks, bottles, pipettes, and stirring rods as PCB-contaminated solid waste.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use only with PCBs.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a PCB-contaminated liquid waste container. Repeat for a total of 5-10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for a minimum of 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements, avoiding the use of plastic containers for QC samples to be analyzed for organic constituents. This procedure describes the preparation of a 500-mL PCBs-in-water QC sample in an amber glass jar.

7.3.2. Remove a vial containing a standard of the desired Aroclor with a concentration of approximately 50 μg/mL from the freezer and allow it to reach room temperature.

7.3.3. Fill a precleaned 500-mL amber bottle to the neck with distilled water. Use only distilled water that has not been stored in plastic or run through plastic tubing.

7.3.4. Using a syringe, spike a volume of the 50-μg/mL Aroclor standard below the surface of the water to reach the desired spike range. Blank QC samples may be made by spiking methanol into the water.

7.3.5. Cap the bottle and label it with a QC sample number.

7.3.6. The analyst will use the entire sample assuming a 500-mL volume.

7.3.7. Return the standard solution to the freezer.

7.3.8. Refrigerate the QC sample pending analysis.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of the concentrated PCB standard prepared from pure Aroclor as in the following example.

8.1.1. If 13.2 mg of pure Aroclor is diluted to 10 mL with methanol, the concentration of PCB in the standard is 1.32 mg/mL.

$$\frac{13.2\ \text{mg}}{10\ \text{mL}} = 1.32\ \text{mg/mL}\ .$$

8.2. Calculate the concentration of the dilution of the PCB standard as in the following example.

8.2.1. If 190 μL of a PCB standard whose concentration is 1.32 mg/mL is diluted to 5 mL with methanol, the concentration of the dilute standard is 50.2 μg/mL.

$$\frac{\left(\frac{1.32\ \text{mg}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(190\ \mu\text{L})\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{5\ \text{mL}} = 50.2\ \mu\text{g/mL}$$

8.3. Calculate the concentration of PCBs in the QC sample as in the following example.

8.3.1. If 150 μL of a 50.2-μg/mL PCB standard is spiked into 500 mL of distilled water, the concentration of PCBs in the QC sample will be 15.1 μg/L.

$$\frac{\left(\frac{50.2\ \mu\text{g}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(150\ \mu\text{L})}{(500\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 15.1\ \mu\text{g/L}\ .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record PCB concentrations in the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate PCB-contaminated solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from solid waste that is not contaminated with PCBs.

9.1.2. Label the can to indicate its use for PCB-contaminated waste.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, identify it as PCB-contaminated waste, and place it in a functioning chemical exhaust hood pending pickup by Waste Services (CST-17).

9.1.5. Put a new plastic bag into the waste can for continued use.

9.2. Liquid waste.

9.2.1. Accumulate PCB-contaminated liquid waste (such as rinses from PCB-contaminated syringes, PCB standards, and incorrectly spiked QC samples) in a covered polyethylene bottle in a secondary containment tray and keep it segregated from liquid waste that is not contaminated with PCBs.

9.2.2. Label the bottle to indicate its use for PCB-contaminated waste.

9.2.3. Open the bottle only for the time necessary to add waste to it.

9.2.4. When the bottle is full, cap it and keep it in the secondary containment tray pending pickup by CST-17.

9.2.5. Label a new bottle for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag or bottle of PCB-contaminated waste by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form (WPF) that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.2. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Polychlorinated Biphenyls," Administrative Requirement 10-4, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked the entire section has been revised.

POLYCHLORINATED BIPHENYLS ON SOIL — QC SAMPLE PREPARATION

Analyte: Polychlorinated biphenyls (PCBs)	**Method No.:** QCO190
Matrix: Soil	**Spike Range:** 10-30 μg/g
Procedure: Analysis by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** EPA standards - 100% ± 10.0% RSD CST-3 standards - 100% ± 1.8% RSD
Effective Date: 05/17/88	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 to 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions of PCB 1242, 1254, and 1260 in hexane or obtain Environmental Protection Agency (EPA) Aroclor 1242, 1254, and 1260 standards. Refer to the table below for Aroclors and associated Chemical Abstract Service (CAS) numbers.

Compound	CAS Number
Aroclor 1242	53469219
Aroclor 1254	11097691
Aroclor 1260	11096825
Total PCBs	1336363

1.2. Spike the Aroclor standard directly onto a soil sample.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, volumetric flask, and balance. A relative standard deviation (RSD) of 10.0% for EPA standards and 1.8% for in-house standards has been calculated for the error of the standard and for the spiking and weighing process based on the following:

2.1.1. EPA standard.

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated results,
M1 = standard error,
M2 = spiking error, and
M3 = weighing error.

2.1.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of microsyringe,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.1.2. In-house standard.

$$U = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7} ,$$

where U = uncertainty,
M1 = standard error,
M2 = first weighing error,
M3 = first dilution error,

M4 = first spiking error,
M5 = second dilution error,
M6 = second spiking error, and
M7 = second weighing error.

2.1.2.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2 + R_{M4}^2 + R_{M5}^2 + R_{M6}^2 + R_{M7}^2} \times 100 ,$$

where SDT = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of first balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of second balance, and
100 = factor to convert to percentage.

2.2. Analyses by GCECD of QC samples prepared between 1990 and 1992 using this procedure are summarized below in Table I. The data are published in Source Materials 10.1 through 10.3.

TABLE I. PCB-ON-SOIL SPIKE RECOVERY DATA (% recovery ± std dev)

	1990 Mean ± std dev	N	1991 Mean ± std dev	N	1992 Mean ± std dev	N
			Soil			
Aroclor 1242	106 ± 36	(19)	90 ± 20	(13)	88 ± 29	(20)
Aroclor 1254	72	(2)	74 ± 28	(7)	63 ± 23	(10)
Aroclor 1260	94 ± 19	(27)	111 ± 29	(16)	84 ± 33	(25)
Total Aroclor	98 ± 27	(48)	96 ± 29	(36)	82 ± 31	(55)

3. Collection and Storage of Samples

3.1. The blank soil matrix and the spiked samples should be stored in glass bottles fitted with Teflon lids. Avoid using plastic containers and lids because phthalates may leach from plastics and contaminate the soil.

3.2. Spiked QC samples are stored at room temperature pending analysis. A study performed in 1989–1990 showed no appreciable difference in analyte recovery between samples stored at room temperature and those stored in the refrigerator.

4. Apparatus

4.1. Syringes: gas-tight, 100-, 250-, and 1000-μL.

4.2. Bottles: 1/2-oz, glass with Teflon-lined lids.

4.3. Vials: 1.5-mL, glass.

4.4. Caps: open-top to fit vials.

4.5. Septa: Teflon/silicone discs to fit open-top caps

4.6. Teflon tape.

4.7. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.8. Pipettes: Pasteur, disposable glass.

4.9. Pipette bulb: rubber, to fit Pasteur pipette.

4.10. Stirring rod: glass, 3- to 4-mm-diam.

4.11. Volumetric flasks: 5-mL, class A, glass.

4.12. Labels printed with QC sample numbers.

5. Reagents

5.1. Hexane (analytical-grade).

5.2. Soil. A clean, dry 10-g aliquot is required for each sample. A suitable soil does not contain the analyte of interest and presents few interferences to the analytical method.

5.3. Blank soil heated to nominally 100°C for 5 h and stored in glass is used as a sample matrix.

6. Calibration and Standards

6.1. EPA Aroclor standards in isooctane or methanol are available in PCB concentrations between 500 and 3000 μg/mL.

6.2. After opening the heat-sealed ampules containing Aroclor standards, transfer the contents into vials with screw caps with Teflon/silicone septa. Wrap the caps with Teflon tape. Remove the original label and affix it to the vial or transfer the standards information to a label on the new vial.

6.3. Solutions of PCBs may be prepared from pure PCBs in concentrations of 50–60 mg/mL.

6.4. Preparation of in-house standards in hexane.

6.4.1. Tare a 5-mL volumetric flask on an analytical balance. Add approximately 250–300 mg of a pure PCB to the bottom of the flask using a glass Pasteur pipette or a glass stirring rod. Record the mass added.

6.4.2. Dissolve the PCB and dilute it to volume with hexane. Mix by inversion.

6.4.3. Prepare a separate standard solution for each PCB desired. Do not mix Aroclors.

6.4.4. The standard concentration will be 50–60 mg/mL. See Step 8.1.

6.4.5. Transfer the standard to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.4.6. Label the vials with information identifying the standard.

6.5. Prepare a 1:10 dilution of the in-house standard in hexane.

6.5.1. Add 4 mL of hexane to a clean 5-mL volumetric flask.

6.5.2. Using a syringe, add 500 μL of 50- to 60-mg/mL Aroclor in-house standard to the hexane in the flask.

6.5.3. Dilute the standard to volume with hexane. Mix by inversion.

6.5.4. The concentration of the dilution will be 5000–6000 μg/mL. See Step 8.2.

6.5.5. Transfer the standard to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.5.6. Label the vials with information identifying the standard.

6.6. Store stock standards in a freezer.

7. Procedure

7.1. Discard used, PCB-contaminated flasks, bottles, and pipettes in the PCB waste container.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use only with PCBs.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements. However, avoid using plastic containers for QC samples that are to be analyzed for organic constituents. This procedure describes the preparation of a PCB-on-soil QC sample using 10 g of blank soil and a 1/2-oz glass bottle.

7.3.2. Accurately weigh 10 g of blank soil into a 1/2-oz glass bottle with a Teflon-lined lid. Record the mass of soil on the bottle with a felt-tipped pen for reference by the analyst.

7.3.3. Remove a vial containing a standard of the desired Aroclor in the concentration range 500–6000 μg/mL from the freezer and allow it to reach room temperature.

7.3.4. Spike a volume of the standard directly onto the soil to reach the desired spike range. Avoid wetting the bottle walls. The analyst will desorb the entire sample in the bottle. See Step 8.3.

7.3.5. Cap the bottle and label it with a QC sample number.

7.3.6. Return the vial containing the Aroclor standard to the freezer.

7.3.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

7.3.8. Store the QC samples at room temperature pending analysis.

8. Calculations

8.1. Calculate the concentration of the concentrated PCB standard prepared from pure PCBs as in the following example.

8.1.1. If 275.0 mg of pure PCB is diluted to 5 mL with hexane, the concentration of the PCB in the standard is 55 mg/mL.

$$\frac{275.0 \text{ mg}}{5 \text{ mL}} = 55 \text{ mg/mL} \quad .$$

8.2. Calculate the concentration of the 1:10 dilution of the concentrated PCB standard as in the following example.

8.2.1. If 500 μL of a PCB standard whose concentration is 55 mg/mL is diluted to 5 mL with hexane, the concentration of the dilute standard is 5500 μg/mL.

$$\frac{(55 \text{ mg/mL}) \left(\frac{1 \text{ mL}}{1000 \ \mu\text{L}}\right) (500 \ \mu\text{L}) \left(\frac{1000 \ \mu\text{g}}{1 \text{ mg}}\right)}{5 \text{ mL}} = 5500 \ \mu\text{g/mL} \quad .$$

8.3. Calculate spike concentrations as in the following example.

8.3.1. If 50 μL of a 5500-μg/mL PCB standard is spiked onto 10.0005 g of soil, the PCB concentration in the QC sample is 27 μg/g.

$$\frac{(5500\ \mu g/mL)\left(\frac{1\ mL}{1000\ \mu L}\right)(50\ \mu L)}{10.0005\ g} = 27\ \mu g/g \quad .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record Aroclor concentrations in the QC samples in μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. PCB-contaminated solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) is accumulated in a covered metal can lined with a plastic bag and is kept segregated from non-PCB-contaminated solid waste.

9.1.2. The can is labeled with a label indicating its use for PCB-contaminated waste.

9.1.3. The can is opened only for the time necessary to add waste.

9.1.4. When the plastic bag is full, it is sealed with tape, removed from the can, identified as PCB-contaminated waste, and placed in a functioning chemical exhaust hood pending pickup by Waste Services (CST-17).

9.1.5. A new plastic bag is put into the waste can for continued use.

9.2. Liquid waste.

9.2.1. PCB-contaminated liquid waste (such as rinses from PCB-contaminated syringes, PCB standards, and incorrectly spiked QC samples) is accumulated in a covered polyethylene bottle in a secondary containment tray and is kept segregated from non-PCB-contaminated liquid waste.

9.2.2. The bottle is labeled with a label indicating its use for PCB-contaminated waste and with a hazardous waste label if the waste contains hazardous components.

9.2.3. The bottle is opened only for the time necessary to add waste.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag or bottle of PCB-contaminated waste by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Polychlorinated Biphenyls," Administrative Requirement 10-4, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

POLYCHLORINATED BIPHENYLS ON SWIPES — QC SAMPLE PREPARATION

Analyte: Polychlorinated biphenyls (PCBs)	**Method No.:** QCO200
Matrix: Gauze swipes	**Spike Range:** 5–20 μg/sample
Procedure: Analysis by gas chromatography with electron-capture detection (GCECD)	**Accuracy and Precision:** EPA standards - 100% ± 10.1% RSD CST-3 standards - 100% ± 5.2% RSD
Effective Date: 06/05/87	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 to 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions of PCB 1242, 1254, and 1260 in hexane or obtain Environmental Protection Agency (EPA) Aroclor 1242, 1254, and 1260 standards. Refer to the table below for Aroclors and associated Chemical Abstract Service (CAS) numbers.

Compound	CAS Number
Aroclor 1242	53469219
Aroclor 1254	11097691
Aroclor 1260	11096825
Total PCBs	1336363

1.2. Spike an Aroclor standard onto a blank 2- × 2-in. gauze in a 1/2-oz bottle. The analyst will desorb the sample in this container.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flasks. A relative standard deviation (RSD) of 10.1% for EPA standards and 5.2% for in-house standards has been calculated for the error of the standard and for weighing, dilution, and spiking, based on the following:

2.1.1. EPA standard.

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = standard error, and
M2 = spiking error.

2.1.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.1.2. In-house standard.

$$U = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5} ,$$

where U = uncertainty,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = spiking error,
M5 = second dilution error, and
M6 = second spiking error.

2.1.2.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6}} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe, and
100 = factor to convert to percentage

2.2. Analyses by GCECD of QC samples prepared between 1990 and 1992 using this procedure are summarized in Table I. The data are published in Source Materials 10.1 through 10.3.

TABLE I. PCB-ON-SWIPES SPIKE RECOVERY DATA
(% recovery ± std dev)

	1990 Mean ± std dev	N	1991 Mean ± std dev	N	1992 Mean ± std dev	N
Aroclor 1242	96 ± 30	(28)	105 ± 34	(25)	86 ± 30	(16)
Aroclor 1254	98 ± 2	(9)	104 ± 30	(26)	112 ± 25	(33)
Aroclor 1260	95 ± 19	(48)	104 ± 27	(31)	89 ± 11	(14)
Total Aroclor	96 ± 24	(85)	104 ± 30	(82)	100 ± 27	(63)

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis. A study performed between 1989 and 1990 showed no appreciable difference in analyte recovery between samples stored at room temperature and those stored in the refrigerator.

3.2. There is no holding time requirement for the analysis of PCB-on-swipe samples.

4. Apparatus

4.1. Syringes: gas-tight, 25-, 50- and 100-μL.

4.2. Bottles: 1/2-oz, glass, with Teflon-lined screw-on lids.

4.3. Gauze pads: 2- × 2-in.

4.4. Vials: 1.5-mL, glass.

4.5. Caps: open-top, to fit 1.5-mL vials.

4.6. Septa: Teflon/silicone discs to fit open-top caps.

4.7. Teflon tape.

4.8. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.9. Pipettes: Pasteur, disposable glass.

4.10. Pipette bulb: rubber, to fit Pasteur pipette.

4.11. Stirring rod: glass, 3- to 4-mm-diam.

4.12. Volumetric flasks: 5-mL, class A, glass.

4.13. Labels printed with QC sample numbers.

5. Reagents

5.1. Hexane (analytical-grade).

6. Calibration and Standards

6.1. EPA Aroclor standards in isooctane or methanol are available in concentrations between 500 and 3000 μg/mL.

6.2. After opening the heat-sealed ampul containing an Aroclor standard, transfer the contents into vials fitted with screw caps with Teflon septa. Wrap the caps with Teflon tape. Remove the original label and affix it to the vial or transfer the standard information to a label on the vial.

6.3. Solutions of PCBs may be prepared from pure PCBs in concentrations of 50–60 mg/mL.

6.4. Preparation of in-house standards in hexane.

6.4.1. Tare a 5-mL volumetric flask on an analytical balance. Add approximately 250–300 mg of a pure PCB to the flask using a glass Pasteur pipette or a glass stirring rod. Record the mass added.

6.4.2. Dissolve the PCB and dilute it to volume with hexane. Mix by inversion.

6.4.3. Prepare a separate standard solution for each PCB desired. Do not mix Aroclors.

6.4.4. The standard concentration will be 50–60 mg/mL. See Step 8.1.

6.4.5. Transfer the standard to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.4.6. Label the vials with information identifying the standard.

6.5. Prepare a 1:100 dilution of the in-house standard in hexane.

6.5.1. Add 4 mL of hexane to a clean 5-mL volumetric flask.

6.5.2. Using a syringe, add 50 μL of a 50- to 60-mg/mL Aroclor in-house standard prepared in Step 6.4 to the hexane in the flask.

6.5.3. Dilute the standard to volume with hexane. Mix by inversion.

6.5.4. The concentration of the dilution will be 0.5–0.6 mg/mL or 500–600 μg/mL. See Step 8.2.

6.5.5. Transfer the standard to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.5.6. Label the vials with information identifying the standard.

6.6. Store the stock standards in a freezer.

7. Procedure

7.1. Discard used, PCB-contaminated flasks, bottles, and pipettes in the PCB waste container.

7.2. Cleaning of syringes.

7.2.1. Dedicate a group of syringes for use only with PCBs.

7.2.2. Fill the syringe with methanol through the needle. Discard the methanol into a waste container. Repeat for a total of 5–10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Remove a vial containing a standard of the desired Aroclor in the concentration range 500–1000 μg/mL from the freezer and allow it to reach room temperature.

7.3.2. Place a 2- × 2-in. blank gauze pad into a clean 1/2-oz bottle fitted with a Teflon-lined cap.

7.3.3. Spike an aliquot of PCB standard directly onto the gauze surface to reach the desired spike range. The analyst will desorb the sample in the bottle. See Step 8.3.

7.3.4. Cap the vial and label it with a QC number.

7.3.5. Return the vial containing the Aroclor standard to the freezer.

7.3.6. Store the QC samples at room temperature pending analysis.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the concentration of the concentrated PCB standard prepared from pure PCBs as in the following example.

8.1.1. If 275.0 mg of pure PCB is diluted to 5 mL with hexane, the concentration of the PCB in the standard is 55 mg/mL.

$$\frac{275.0\ \text{mg}}{5\ \text{mL}} = 55\ \text{mg/mL} \quad .$$

8.2. Calculate the concentration of the 1:100 dilution of the concentrated PCB standard as in the following example.

8.2.1. If 50 μL of a PCB standard whose concentration is 55 mg/mL is diluted to 5 mL with hexane, the concentration of the dilute standard is 550 μg/mL.

$$\frac{(55\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(50\ \mu\text{L})\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{5\ \text{mL}} = 550\ \mu\text{g/mL} \quad .$$

8.3. Calculate the concentration of PCB spiked onto a gauze sample as in the following example.

8.3.1. If 24 μL of a 550-μg/mL PCB standard is spiked onto a gauze square, the PCB concentration in the QC sample is 13 μg/sample.

$$\frac{(550\ \mu\text{g/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(24\ \mu\text{L})}{\text{sample}} = 13\ \mu\text{g/sample} \quad .$$

8.3.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4. Record Aroclor concentrations in μg/sample.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. PCB-contaminated solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples) is accumulated in a covered metal can lined with a plastic bag and is kept segregated from non-PCB-contaminated solid waste.

9.1.2. The can is labeled with a label indicating its use for PCB-contaminated waste.

9.1.3. The can is opened only for the time necessary to add waste to it.

9.1.4. When the plastic bag is full, it is sealed with tape, removed from the can, identified as PCB-contaminated waste, and placed in a functioning chemical exhaust hood pending pickup by Waste Services (CST-17).

9.1.5. A new plastic bag is put into the waste can for continued use.

9.2. Liquid waste.

9.2.1. PCB-contaminated liquid waste (such as rinses from PCB-contaminated syringes, PCB standards, and incorrectly spiked QC samples) is accumulated in a covered polyethylene bottle in a secondary containment tray and is kept segregated from non-PCB-contaminated liquid waste.

9.2.2. The bottle is labeled with a label indicating its use for PCB-contaminated waste and with a hazardous waste label if the waste contains hazardous components.

9.2.3. The bottle is opened only for the time necessary to add waste.

9.2.4. When the bottle is full, it is capped and kept in the secondary containment tray pending pickup by CST-17.

9.2.5. A new bottle is labeled for further use.

9.3. Waste pickup.

9.3.1. Request CST-17 pick up a full bag or bottle of PCB-contaminated waste by using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Polychlorinated Biphenyls," Administrative Requirement 10-4, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL — QC SAMPLE PREPARATION

Analyte: Semivolatile organic compounds	**Method No.** QCO210
Matrix: Soil	**Spike Range:** 0.67 - 6.67 mg/kg
Procedure: Gas chromatography and mass spectrometry (GCMS)	**Accuracy and Precision:** 100% ± 5.2% RSD
Effective Date: 01/22/90	**Authors:** Nancy L. Koski Margaret A. Gautier Carol R. Sutcliffe

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions in acetone of 4-10 semivolatile compounds chosen primarily from the list in Table I, found at the end of the procedure.

1.2. Spike the stocks onto 30 g of blank soil.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask, microsyringe, and balance. A relative standard deviation (RSD) of 5.2% at the 1-σ level has been calculated for the error of the standard and for spiking, weighing, and dilution based on the following:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5},$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = spiking error, and
M5 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe,
R^2_{M5} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analysis by GCMS of QC samples prepared between 1990 and 1991 using this procedure are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL SPIKE RECOVERY DATA

	1990			1991		
Compound	Mean	± std dev	(n)	Mean	± std dev	(n)
Acenaphthene		—		62		(1)
Acenaphthylene		—			—	
Aniline	10	± 4	(3)		—	
Anthracene	80	± 28	(12)	85	± 10	(8)
Azobenzene		—			—	
Benzo[a]anthracene		—			—	
Benzo[b]fluoranthene	98		(2)	78	± 9	(3)
Benzo[k]fluoranthene		—			—	

TABLE II. SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL SPIKE RECOVERY DATA (cont.)

Compound	1990 Mean	±	std dev	(n)	1991 Mean	±	std dev	(n)
Benzoic acid	50	±	37	(8)	20	±	7	(3)
Benzo[g,h,i]perylene	—				—			
Benzo[a]pyrene	—				60			(1)
Benzyl alcohol	62	±	16	(4)	73	±	37	(8)
Bis(2-chloroethoxy)methane	—				—			
Bis(2-chloroethyl)ether	67	±	9	(5)	79	±	12	(4)
Bis(2-chloroisopropyl)ether	—				—			
Bis(2-ethylhexyl)phthalate	—				—			
4-Bromophenyl phenylether	—				—			
Butyl benzyl phthalate	—				—			
4-Chloroaniline	—				—			
4-Chloro-3-methylphenol	—				76	±	16	(5)
2-Chloronaphthalene	—				58	±	12	(6)
2-Chlorophenol	—				58	±	10	(3)
4-Chlorophenyl phenyl ether	—				—			
Chrysene	—				135	±	60	(4)
Di-n-butyl phthalate	—				67	±	4	(6)
Di-n-octyl phthalate	—				124	±	91	(3)
Dibenzo[a,h]anthracene	—				—			
Dibenzofuran	—				—			
1,2-Dichlorobenzene	—				94	±	11	(11)
1,3-Dichlorobenzene	—				—			
1,4-Dichlorobenzene	9			(1)	57	±	9	(4)
2,4-Dichlorophenol	66			(2)	62	±	14	(6)
Diethyl phthalate	111	±	33	(12)	69			(1)
2,4-Dimethylphenol	35			(2)	58	±	12	(5)
Dimethyl phthalate	78			(2)	—			
4,6-Dinitro-2-methylphenol	—				—			
2,4-Dinitrophenol	—				—			
2,4-Dinitrotoluene	—				88			(1)
2,6-Dinitrotoluene	—				68			(1)
Fluoranthene	—				93	±	12	(8)
Fluorene	—				—			
Hexachlorobenzene	54			(1)	—			
Hexachlorobutadiene	59	±	18	(12)	66	±	18	(8)
Hexachlorocyclopentadiene	36			(1)	64			(2)
Hexachloroethane	9			(1)	51	±	27	(4)
Indeno[1,2,3-cd]pyrene	—				—			
Isophorone	64	±	18	(11)	—			
2-Methylnaphthalene	—				—			

TABLE II. SEMIVOLATILE ORGANIC COMPOUNDS ON SOIL SPIKE RECOVERY DATA (cont.)

Compound	1990 Mean	±	std dev	(n)	1991 Mean	±	std dev	(n)
2-Methylphenol	—				—			
4-Methylphenol	—				—			
Naphthalene	55	±	20	(3)	55	±	5	(3)
2-Nitroaniline	—				—			
3-Nitroaniline	—				23	±	11	(3)
4-Nitroaniline	39	±	23	(3)	31	±	13	(4)
Nitrobenzene	59			(2)	—			
2-Nitrophenol	—				—			
4-Nitrophenol	77	±	32	(5)	75	±	15	(11)
N-Nitrosodiphenylamine	—				77			(1)
N-Nitrosodi-n-propylamine	—				—			
Pentachlorophenol	—				—			
Phenanthrene	89			(2)	—			
Phenol	64	±	9	(6)	—			
Pyrene	—				—			
1,2,4-Trichlorobenzene	—				—			
2,4,5-Trichlorophenol	74	±	11	(3)	—			
2,4,6-Trichlorophenol	—				—			

3. Collection and Storage of Samples

3.1. The blank soil matrix and the spiked samples should be stored in glass bottles fitted with Teflon-lined lids. Avoid using plastic containers and lids because phthalates, which are semivolatile compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for the analysis of semivolatile compounds in soil is 14 days.

4. Apparatus

4.1. Volumetric flask: 5-mL, class A, glass.

4.2. Syringes: gas-tight, 25-, 50-, 100-, and 250-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Pipette bulb: rubber, to fit Pasteur pipette.

4.6. Vials: 1.5-mL, glass.

4.7. Caps: open-top, to fit vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Bottles: 2-oz, glass, with Teflon-lined caps.

4.11. Analytical balance: 200-g minimum capacity, 0.1-mg accuracy.

4.12. Laboratory oven: capable of sustaining 100-150°C.

4.13. Labels printed with QC sample numbers.

5. Reagents

5.1. Soil. A clean, dry 30-g aliquot is required for each sample. A suitable soil does not contain the analyte of interest and presents few interferences to the analytical method.

5.2. Blank soil, heated to nominally 100°C for 5 h and stored in glass, is used as a sample matrix.

5.3. Acetone (analytical-grade).

5.4. Methanol (analytical-grade).

5.5. Methylene chloride (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade semivolatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19387). Use both acid and base/neutral semivolatile analytes because the two fractions are extracted separately before being recombined for analysis. Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8-12 mg of a solid semivolatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.2. Add approximately 2 mL of acetone to the flask, stopper the flask, and swirl it to see if all analytes will dissolve. If not, methylene chloride and/or methanol may be added to effect total dissolution. For example, chrysene requires methylene chloride and methanol and gentle heating to effect total dissolution.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8-12 mg in 5 mL of stock solution. See Step 8.2.

6.1.5. Using a syringe, add a liquid analyte just above the surface of the acetone. Stopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte.

6.1.6. Dilute the solution to volume with acetone. Mix by inversion.

6.1.7. Discard the solution in the neck of the flask to minimize concentration changes due to loss of analytes from the surface of the solution.

6.1.8. The concentration of analytes in the stock solution will be 1.5-2.5 mg/mL.

6.1.9. Transfer the stock solution to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.10. Label the vials with information identifying the standard and with the expiration date.

6.1.11. The standard solution in acetone is stable for approximately 3 months stored at -20°C.

6.2. Prepare additional stock solution using different analytes selected primarily from Table I. The number of analytes in the QC sample may be increased by using more than one stock solution to spike the sample.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store glassware in a laboratory oven maintained at 100-150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with semivolatile compounds.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5-10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for approximately 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Remove a vial of semivolatile stock solution from the freezer and allow it to come to room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.2. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.3. Accurately weigh 30 g of blank soil into a 2-oz glass bottle. Record the mass of soil on the bottle with a felt-tipped pen for reference by the analyst.

7.3.4. Using a gas-tight syringe, spike a volume of the standard onto the surface of the soil to reach the desired spike range. Blank QC samples may be prepared by spiking acetone onto the soil. The analyst will use the entire sample.

7.3.5. Cap the vial with a Teflon-lined lid and label it with a QC number.

7.3.6. Return the stock solution to the freezer.

7.3.7. Refrigerate the QC sample pending analysis. The maximum holding time for semivolatile organic compounds on soil QC samples is 14 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Use 8-12 mg of a solid analyte in 5.0 mL of stock solution.

8.2. Calculate the volume of neat liquid analyte needed to prepare a stock solution in the range of 8-12 mg/5 mL.

8.2.1. Read the density of the neat liquid analyte from Table I. The density of nitrobenzene is 1.196 mg/μL.

8.2.2. The desired weight spike range for 5 mL of stock solution is 8-12 mg of neat analyte.

8.2.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} = 6.7 \text{ to } 10.0\ \mu\text{L}$$

For nitrobenzene, between 6.7 and 10 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5-2.5 mg/mL in the stock solution.

8.3. Calculate the concentration of each analyte in the stock solution as in the following examples.

8.3.1. If 9.6 mg of solid anthracene is dissolved in 5.0 mL of stock solution, the concentration of anthracene in the stock solution is 1.92 mg/mL.

$$\frac{9.6\ \text{mg}}{5.0\ \text{mL}} = 1.92\ \text{mg/mL}$$

8.3.2. If 9 μL of liquid nitrobenzene, weighing 10.8 mg, is diluted in 5 mL of stock solution, the concentration of nitrobenzene in the stock solution is 2.16 mg/mL.

$$\frac{10.8\ \text{mg}}{5\ \text{mL}} = 2.16\ \text{mg/mL}$$

8.4. Calculate the concentration of each analyte in the QC sample as in the following example.

8.4.1. If 60 μL of a stock standard solution containing 1.92 mg/mL of anthracene and 2.16 mg/mL of nitrobenzene is spiked onto 30.0018 g of

blank soil, the concentration of anthracene in the QC sample will be 3.84 mg/kg. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1.92\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)}{30.0018\ \text{g}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)} = 3.84\ \text{mg/kg}$$

The concentration of nitrobenzene in the QC sample will be 4.32 mg/kg. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2.16\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)}{30.0018\ \text{g}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)} = 4.32\ \text{mg/kg}$$

8.5. Record the analyte concentrations in the QC sample in mg/kg or μg/g.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Management (CST-7).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full, and keep the can in the secondary containment tray pending pickup by CST-7.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full, and keep the jar in the secondary containment tray pending pickup by CST-7.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up a full bag, can, or jar of waste contaminated with organic compounds using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	CAS No.	Category	Density of liquid, (mg/μL)
acenaphthene	83329	Base/Neutral	solid
acenaphthylene	208968	Base/Neutral	0.899
aniline	62533	Base/Neutral	1.022
anthracene	120127	Base/Neutral	solid
azobenzene	103333	Base/Neutral	1.090
benz[a]anthracene	56553	Base/Neutral	solid
m-benzidine	92875	Base/Neutral	solid
benzo[b]fluoranthene	205992	Base/Neutral	solid
benzo[k]fluoranthene	207089	Base/Neutral	solid
benzoic acid	65850	Acid	solid
benzo[g,h,i]perylene	191242	Base/Neutral	solid
benzo[a]pyrene	50328	Base/Neutral	solid
benzyl alcohol	100516	Base/Neutral	1.045
bis(2-chloroethoxy)methane	111911	Base/Neutral	solid
bis(2-chloroethyl)ether	111444	Base/Neutral	1.220
bis(2-chloroisopropyl)ether	108601	Base/Neutral	solid
bis(2-ethylhexyl) phthalate	117817	Base/Neutral	0.981
4-bromophenyl phenyl ether	101553	Base/Neutral	1.423
butyl benzyl phthalate	85687	Base/Neutral	0.966
4-chloroaniline	106478	Base/Neutral	solid
4-chloro-3-methylphenol	59507	Acid	solid
2-chloronaphthalene	91587	Base/Neutral	solid
2-chlorophenol	95578	Acid	1.241
4-chlorophenyl phenyl ether	7005723	Base/Neutral	solid
chrysene	218019	Base/Neutral	solid
di-n-butyl phthalate	84742	Base/Neutral	1.043
di-n-octyl phthalate	117840	Base/Neutral	0.981
dibenz[a,h]anthracene	53703	Base/Neutral	solid
dibenzofuran	132649	Base/Neutral	solid
1,2-dichlorobenzene	95501	Base/Neutral	1.306
1,3-dichlorobenzene	541731	Base/Neutral	1.288
1,4-dichlorobenzene	106467	Base/Neutral	1.241
3,3'-dichlorobenzidine	91941	Base/Neutral	solid
2,4-dichlorophenol	120832	Acid	solid
diethyl phthalate	84662	Base/Neutral	1.118
2,4-dimethylphenol	105679	Acid	1.027
dimethyl phthalate	131113	Base/Neutral	1.190
4,6-dinitro-2-methylphenol	534521	Acid	solid

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS (cont)

Analyte	CAS No.	Category	Density of liquid, (mg/μL)
2,4-dinitrophenol	51285	Acid	solid
2,4-dinitrotoluene	121142	Base/Neutral	solid
2,6-dinitrotoluene	606202	Base/Neutral	solid
fluoranthene	206440	Base/Neutral	solid
fluorene	86737	Base/Neutral	solid
hexachlorobenzene	118741	Base/Neutral	solid
hexachlorobutadiene	87683	Base/Neutral	1.665
hexachlorocyclopentadiene	77474	Base/Neutral	1.702
hexachloroethane	67721	Base/Neutral	2.091
indeno[1,2,3-cd]pyrene	193395	Base/Neutral	solid
isophorone	78591	Base/Neutral	0.923
2-methylnaphthalene	91576	Base/Neutral	1.000
2-methylphenol	95487	Acid	1.048
4-methylphenol	106445	Acid	1.034
naphthalene	91203	Base/Neutral	solid
2-nitroaniline	88744	Base/Neutral	solid
3-nitroaniline	99092	Base/Neutral	solid
4-nitroaniline	100016	Base/Neutral	solid
nitrobenzene	98953	Base/Neutral	1.196
2-nitrophenol	88755	Acid	solid
4-nitrophenol	100027	Acid	solid
N-nitrosodimethylamine	62759	Base/Neutral	1.006
N-nitrosodiphenylamine	86306	Base/Neutral	solid
N-nitrosodi-n-propylamine	621647	Base/Neutral	solid
pentachlorophenol	87865	Acid	1.978
phenanthrene	85018	Base/Neutral	solid
phenol	108952	Acid	solid
pyrene	129000	Base/Neutral	solid
1,2,4-trichlorobenzene	120821	Base/Neutral	1.454
2,4,5-trichlorophenol	95954	Acid	solid
2,4,6-trichlorophenol	88062	Acid	solid

SEMIVOLATILE ORGANIC COMPOUNDS IN WATER — QC SAMPLE PREPARATION

Analyte: Semivolatile organic compounds	**Method No.:** QCO220
Matrix: Water	**Spike Range:** 20-200 μg/L
Procedure: Gas chromatography and mass spectrometry (GCMS)	**Accuracy and Precision:** 100% ± 5.2% RSD
Effective Date: 01/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier Carol Sutcliffe

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare stock solutions of 4-10 semivolatile compounds in acetone selected primarily from the list in Table I, found at the end of this procedure.

1.2. Spike the stocks into 1 L of distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 5.2% at the 1-σ level has been calculated for the error of the standard and for spiking, weighing, and dilution based on the following:

$$D = \frac{M1 \times M2 \times M4}{M3 \times M5} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = pipette error, and
M5 = second dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots . M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$\%S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of microsyringe, and
100 = factor to convert to percentage.

2.2. Analyses by GCMS of QC samples prepared between 1990 and 1991 using this procedure are summarized in Table II below. The data are published in Source Materials 10.1 and 10.2.

TABLE II. SEMIVOLATILE ORGANIC COMPOUNDS IN WATER SPIKE RECOVERY DATA

Compound	1990 Mean ± std dev	(n)	1991 Mean ± std dev	(n)
Acenaphthene	—		84 ± 18	(4)
Acenaphthylene	—		—	
Aniline	84 ± 19	(4)	88	(1)
Anthracene	58 ± 15	(5)	—	
Azobenzene	—		—	
Benzo[a]anthracene	—		—	

TABLE II. SEMIVOLATILE ORGANIC COMPOUNDS IN WATER SPIKE RECOVERY DATA (cont)

Compound	1990 Mean	±	std dev	(n)	1991 Mean	±	std dev	(n)
Benzo[b]fluoranthene		—			85			(2)
Benzo[k]fluoranthene		—				—		
Benzoic acid	54	±	35	(9)	57	±	43	(4)
Benzo[g,h,i]perylene		—				—		
Benzo[a]pyrene		—			40			(2)
Benzyl alcohol	53	±	29	(4)	79	±	22	(6)
Bis(2-chloroethoxy)methane		—				—		
Bis(2-chloroethyl)ether	63	±	7	(4)	60	±	19	(4)
Bis(2-chloroisopropyl)ether		—				—		
Bis(2-ethylhexyl)phthalate		—				—		
4-Bromophenyl phenyl ether		—				—		
Butyl benzyl phthalate		—				—		
4-Chloroaniline		—				—		
4-Chloro-3-methylphenol		—			67	±	29	(4)
2-Chloronaphthalene		—			60			(2)
2-Chlorophenol		—			60	±	15	(4)
4-Chlorophenyl phenyl ether		—				—		
Chrysene		—			16			(1)
Di-n-butyl phthalate		—			29			(2)
Di-n-octyl phthalate		—			66	±	15	(4)
Dibenzo[a,h]anthracene		—				—		
Dibenzofuran		—				—		
1,2-Dichlorobenzene		—				—		
1,3-Dichlorobenzene		—				—		
1,4-Dichlorobenzene		—			31			(2)
2,4-Dichlorophenol	58			(2)	67			(2)
Diethyl phthalate	46	±	56	(4)	15			(2)
2,4-Dimethylphenol		—			70	±	15	(6)
Dimethyl phthalate		—				—		
4,6-Dinitro-2-methylphenol		—				—		
2,4-Dinitrophenol		—				—		
2,4-Dinitrotoluene		—				—		
2,6-Dinitrotoluene		—			42	±	25	(4)
Fluoranthene		—			78	±	19	(6)
Fluorene		—				—		
Hexachlorobenzene	64	±	6	(3)		—		
Hexachlorobutadiene	47	±	6	(5)	50	±	6	(4)
Hexachlorocyclopentadiene	48			(2)	46	±	12	(4)
Hexachloroethane	48			(2)		—		
Indeno[1,2,3-cd]pyrene		—				—		

TABLE II. SEMIVOLATILE ORGANIC COMPOUNDS IN WATER SPIKE RECOVERY DATA (cont)

Compound	1990 Mean ± std dev	(n)	1991 Mean ± std dev	(n)
Isophorone	69 ± 13	(5)	—	
2-Methylnaphthalene	—		—	
2-Methylphenol	—		—	
4-Methylphenol	—		—	
Naphthalene	—		58	(2)
2-Nitroaniline	—		—	
3-Nitroaniline	—		70	(2)
4-Nitroaniline	—		80 ± 17	(4)
Nitrobenzene	—		—	
2-Nitrophenol	—		—	
4-Nitrophenol	85 ± 23	(6)	62 ± 20	(8)
N-Nitrosodiphenylamine	—		42 ± 27	(4)
N-Nitrosodi-n-propylamine	—		—	
Pentachlorophenol	92 ± 27	(6)	—	
Phenanthrene	64	(2)	—	
Phenol	49 ± 14	(4)	66	(2)
Pyrene	—		—	
1,2,4-Trichlorobenzene	—		—	
2,4,5-Trichlorophenol	74 ± 17	(10)	—	
2,4,6-Trichlorophenol	—		—	

3. Collection and Storage of Samples

3.1. Distilled water is used as the blank matrix. Use water that has not been run through plastic tubing or stored in plastic holding vessels because phthalates, which are semivolatile organic compounds, may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for semivolatiles in water is 7 days.

4. Apparatus

4.1. Volumetric flasks: 5-mL, class A, glass.

4.2. Syringes: gas-tight, 25-, 50-, 100-, and 250-μL.

4.3. Spatulas.

4.4. Pipettes: Pasteur, glass.

4.5. Pipette bulb: rubber, to fit Pasteur pipette.

4.6. Vials: 1.5-mL, glass.

4.7. Caps: open-top, to fit vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Bottles: 1-L wide-mouth glass jars, amber, pre-cleaned, with Teflon-lined lids.

4.11. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.12. Laboratory oven: capable of sustaining 100-150°C.

4.13. Labels: printed with QC sample numbers.

5. Reagents

5.1. Acetone (analytical-grade).

5.2. Methanol (analytical-grade).

5.3. Methylene chloride (analytical-grade).

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade semivolatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Use both acid and base/neutral semivolatile analytes because the two fractions are extracted separately before being recombined for analysis. Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8-12 mg of a solid semivolatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.2. Add approximately 2 mL of acetone to the flask, stopper the flask, and swirl it to see if all analytes will dissolve. If not, methylene chloride and/or methanol may be added to effect total dissolution. For example, chrysene requires methylene chloride and methanol and gentle heating to effect total dissolution.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8-12 mg in 5 mL of stock solution. See Step 8.2.

6.1.5. Using a syringe, add a liquid analyte just above the surface of the acetone. Stopper the flask and record the mass and volume of analyte added. Tare the balance. Repeat for each liquid analyte added.

6.1.6. Dilute the solution to volume with acetone. Mix by inversion.

6.1.7. Discard the solution in the neck of the flask to minimize concentration changes due to loss of analytes from the surface of the solution.

6.1.8. The concentration of analytes in the stock solution will be 1.5-2.5 mg/mL.

6.1.9. Transfer the stock solution to vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.10. Label the vials with information identifying the standard and with the expiration date.

6.1.11. The stock solution in acetone is stable for approximately 3 months stored at -20°C.

6.2. Prepare additional stock solutions using different analytes selected primarily from Table I. The number of analytes in the QC sample may be increased by using more than one solution to spike the sample.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store glassware in a laboratory oven maintained at 100-150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with semivolatile compounds.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5-10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for approximately 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Remove a vial of semivolatile stock solution from the freezer and allow it to come to room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.2. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.3. Fill a pre-cleaned 1-L amber bottle to the neck with distilled water. Use only distilled water that has not been stored in plastic or run through plastic tubing.

7.3.4. Using a syringe, spike a volume of the solution below the surface of the water to reach the desired spike range. Blank QC samples may be prepared by spiking acetone into the water. The analyst will use the entire sample assuming a 1-L volume.

7.3.5. Cap the bottle and label it with a QC sample number.

7.3.6. Return the stock solution to the freezer.

7.3.7. Refrigerate the QC sample pending analysis. The maximum holding time for semivolatile organic compounds in water QC samples is 7 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Use 8-12 mg of a solid analyte in 5.0 mL of stock solution.

8.2. Calculate the volume of a neat liquid analyte needed to prepare a stock solution in the range of 8-12 mg/5 mL.

8.2.1. Read the density of the neat liquid analyte from Table I. The density of nitrobenzene is 1.196 mg/μL.

8.2.2. The desired weight spike range for 5 mL of stock solution is 8-12 mg of neat analyte.

8.2.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}}\ \text{to}\ \frac{12\ \text{mg}}{1.196\ \text{mg}/\mu\text{L}} = 6.7\ \text{to}\ 10.0\ \mu\text{L}$$

For nitrobenzene, between 6.7 and 10 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5-2.5 mg/mL in the stock solution.

8.3. Calculate the concentration of each analyte in the stock solution as in the following examples.

8.3.1. If 9.6 mg of solid anthracene is dissolved in 5.0 mL of stock solution, the concentration of anthracene in the stock solution is 1.92 mg/mL.

$$\frac{9.6\ \text{mg}}{5.0\ \text{mL}} = 1.92\ \text{mg/mL}$$

8.3.2. If 9 μL of liquid nitrobenzene, weighing 10.8 mg, is diluted in 5 mL of stock solution, the concentration of nitrobenzene in the stock solution is 2.16 mg/mL.

$$\frac{10.8\ \text{mg}}{5\ \text{mL}} = 2.16\ \text{mg/mL}$$

8.4. Calculate the concentration of each analyte in the QC sample as in the following example.

8.4.1. If 60 μL of a stock standard solution containing 1.92 mg/mL of anthracene and 2.16 mg/mL of nitrobenzene is spiked into 1 L of distilled water, the concentration of anthracene in the QC sample will be 115 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(1.92\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{1\ \text{L}} = 115\ \mu\text{g/L}$$

The concentration of nitrobenzene in the QC sample will be 130 μg/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2.16\ \text{mg/mL})\ (60\ \mu\text{L})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)}{1\ \text{L}} = 130\ \mu\text{g/L}$$

8.5. Record the analyte concentrations in the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Management (CST-7).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full, and keep the can in the secondary containment tray pending pickup by CST-7.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full, and keep the jar in the secondary containment tray pending pickup by CST-7.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up a full bag, can, or jar of waste contaminated with organic compounds using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	CAS No.	Category	Density of liquid, (mg/μL)
acenaphthene	83329	Base/Neutral	solid
acenaphthylene	208968	Base/Neutral	0.899
aniline	62533	Base/Neutral	1.022
anthracene	120127	Base/Neutral	solid
azobenzene	103333	Base/Neutral	1.090
benz[a]anthracene	56553	Base/Neutral	solid
m-benzidine	92875	Base/Neutral	solid
benzo[b]fluoranthene	205992	Base/Neutral	solid
benzo[k]fluoranthene	207089	Base/Neutral	solid
benzoic acid	65850	Acid	solid
benzo[g,h,i]perylene	191242	Base/Neutral	solid
benzo[a]pyrene	50328	Base/Neutral	solid
benzyl alcohol	100516	Base/Neutral	1.045
bis(2-chloroethoxy)methane	111911	Base/Neutral	solid
bis(2-chloroethyl)ether	111444	Base/Neutral	1.220
bis(2-chloroisopropyl)ether	108601	Base/Neutral	solid
bis(2-ethylhexyl) phthalate	117817	Base/Neutral	0.981
4-bromophenyl phenyl ether	101553	Base/Neutral	1.423
butyl benzyl phthalate	85687	Base/Neutral	0.966
4-chloroaniline	106478	Base/Neutral	solid
4-chloro-3-methylphenol	59507	Acid	solid
2-chloronaphthalene	91587	Base/Neutral	solid
2-chlorophenol	95578	Acid	1.241
4-chlorophenyl phenyl ether	7005723	Base/Neutral	solid
chrysene	218019	Base/Neutral	solid
di-n-butyl phthalate	84742	Base/Neutral	1.043
di-n-octyl phthalate	117840	Base/Neutral	0.981
dibenz[a,h]anthracene	53703	Base/Neutral	solid
dibenzofuran	132649	Base/Neutral	solid
1,2-dichlorobenzene	95501	Base/Neutral	1.306
1,3-dichlorobenzene	541731	Base/Neutral	1.288
1,4-dichlorobenzene	106467	Base/Neutral	1.241
3,3'-dichlorobenzidine	91941	Base/Neutral	solid
2,4-dichlorophenol	120832	Acid	solid
diethyl phthalate	84662	Base/Neutral	1.118
2,4-dimethylphenol	105679	Acid	1.027
dimethyl phthalate	131113	Base/Neutral	1.190
4,6-dinitro-2-methylphenol	534521	Acid	solid

TABLE I. SEMIVOLATILE ORGANIC COMPOUNDS (cont)

Analyte	CAS No.	Category	Density of liquid, mg/μL
2,4-dinitrophenol	51285	Acid	solid
2,4-dinitrotoluene	121142	Base/Neutral	solid
2,6-dinitrotoluene	606202	Base/Neutral	solid
fluoranthene	206440	Base/Neutral	solid
fluorene	86737	Base/Neutral	solid
hexachlorobenzene	118741	Base/Neutral	solid
hexachlorobutadiene	87683	Base/Neutral	1.665
hexachlorocyclopentadiene	77474	Base/Neutral	1.702
hexachloroethane	67721	Base/Neutral	2.091
indeno[1,2,3-cd]pyrene	193395	Base/Neutral	solid
isophorone	78591	Base/Neutral	0.923
2-methylnaphthalene	91576	Base/Neutral	1.000
2-methylphenol	95487	Acid	1.048
4-methylphenol	106445	Acid	1.034
naphthalene	91203	Base/Neutral	solid
2-nitroaniline	88744	Base/Neutral	solid
3-nitroaniline	99092	Base/Neutral	solid
4-nitroaniline	100016	Base/Neutral	solid
nitrobenzene	98953	Base/Neutral	1.196
2-nitrophenol	88755	Acid	solid
4-nitrophenol	100027	Acid	solid
N-nitrosodimethylamine	62759	Base/Neutral	1.006
N-nitrosodiphenylamine	86306	Base/Neutral	solid
N-nitrosodi-n-propylamine	621647	Base/Neutral	solid
pentachlorophenol	87865	Acid	1.978
phenanthrene	85018	Base/Neutral	solid
phenol	108952	Acid	solid
pyrene	129000	Base/Neutral	solid
1,2,4-trichlorobenzene	120821	Base/Neutral	1.454
2,4,5-trichlorophenol	95954	Acid	solid
2,4,6-trichlorophenol	88062	Acid	solid

VOLATILE ORGANIC COMPOUNDS ON SOIL — QC SAMPLE PREPARATION

Analyte: Volatile organic compounds	**Method No.:** QCO250
Matrix: Ottawa sand	**Spike Range:** 100-200 μg/kg
Procedure: Analysis by purge-and-trap extraction, gas chromatography and mass spectrometry (PTGC)	**Accuracy and Precision:** 100% ± 2.0% RSD
Effective Date: 03/19/91	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in methanol of 3 to 6 volatile organic compounds chosen primarily from the list in Table I, found at the end of this procedure.

1.2. Spike the stock solution into methanol.

1.3. The methanol stock dilution is spiked onto the soil matrix immediately before analysis.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with the use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 2.0% at the 1-σ level has been calculated for the error of the standard and for spiking, weighing, and dilution based on the following:

$$D1 = \frac{M1 \times M2}{M3} ,$$

$$D2 = \frac{\left(\frac{D1 \times M5}{(D1 \times M5) + M4}\right) \times M6}{M7} ,$$

$$D3 = \frac{(M3 \times M4)^2}{((M1 \times M2 \times M5) + (M3 \times M4))^2} ,$$

where D1 = first dilution calculated result,
D2 = final calculated result,
D3 = factor for percent relative standard deviation formula in section 2.1.2,
M1 = standard error,
M2 = weighing error,
M3 = dilution error,
M4 = first pipetting error,
M5 = second pipetting error,
M6 = third pipetting error, and
M7 = weighing error.

2.1.1. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$,
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation:

$$S_{D_T} = \sqrt{R^2_{M7} + R^2_{M6} + ((R^2_{M1} + R^2_{M2} + R^2_{M3} + R_{M4} + R_{M5}) \times D3)} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of volumetric flask,
R^2_{M4} = relative variance of first microsyringe,

R^2_{M5} = relative variance of second microsyringe,
R^2_{M6} = relative variance of third microsyringe,
R^2_{M7} = relative variance of balance,
D3 = factor above, and
100 = factor to convert to percentage.

2.2. Analytical results from samples prepared between 1990 and 1991 using this procedure and analyzed by purge-and-trap extraction, gas chromatography and mass spectrometry, are summarized in Table II below. The data are published in Source Materials 10.1 through 10.4.

TABLE II. VOLATILE ORGANIC COMPOUNDS ON SOIL RECOVERY DATA

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
Acetone		—		44	± 17	(27)
Benzene	64	± 30	(4)	34		(1)
Bromobenzene		—		92	± 18	(14)
Bromochloromethane	52		(1)		—	
Bromodichloromethane		—		103	± 25	(11)
Bromoform		—		95	± 26	(9)
Bromomethane		—			—	
2-Butanone (MEK)	110	± 72	(12)	52	± 22	(13)
n-Butylbenzene	24		(1)		—	
sec-Butylbenzene		—			—	
tert-Butylbenzene		—			—	
Carbon disulfide	34	± 14	(3)	37		(1)
Carbon tetrachloride	59	± 34	(5)	102	± 48	(11)
Chlorobenzene	53	± 23	(9)	85	± 18	(15)
Chlorodibromomethane	57	± 29	(5)	97	± 22	(17)
Chloroethane		—			—	
Chloroform		—		79	± 28	(8)
2-Chlorotoluene		—		88	± 36	(6)
4-Chlorotoluene		—			—	
1,2-Dibromo-3-chloropropane		—			—	
1,2-Dibromoethane	29		(2)		—	
Dibromomethane		—		82	± 23	(8)
1,2-Dichlorobenzene		—		94	± 11	(11)
1,3-Dichlorobenzene		—			—	
1,4-Dichlorobenzene	9		(1)	57	± 9	(4)
1,1-Dichloroethane	56	± 21	(8)	26	± 16	(3)
1,2-Dichloroethane	66	± 25	(10)	97	± 42	(14)
1,1-Dichloroethene		—			—	

TABLE II. VOLATILE ORGANIC COMPOUNDS ON SOIL RECOVERY DATA (cont)

Compound	1990 Mean	± std dev	(n)	1991 Mean	± std dev	(n)
cis-1,2-Dichloroethene		—			—	
trans-1,2-Dichloroethene		—			—	
1,2-Dichloropropane	77		(1)	73	± 38	(7)
1,3-Dichloropropane		—			—	
2,2-Dichloropropane		—			—	
1,1-Dichloropropene		—			—	
cis-1,3-Dichloropropene	36	± 22	(5)		—	
trans-1,3-Dichloropropene	93	± 51	(5)		—	
Ethylbenzene	51	± 24	(11)	76	± 31	(9)
2-Hexanone	138	± 67	(8)	69	± 22	(9)
Isopropylbenzene		—			—	
p-Isopropyltoluene		—			—	
Methylene chloride		—		83	± 53	(27)
4-Methyl-2-pentanone (MIK)		—		94	± 20	(14)
n-Propylbenzene	32		(1)	67	± 22	(5)
Styrene	36		(2)	84	± 22	(14)
1,1,1,2-Tetrachloroethane	57		(1)	85	± 18	(5)
1,1,2,2-Tetrachloroethane		—		104	± 16	(11)
Tetrachloroethene	46	± 24	(12)	75	± 28	(15)
Toluene	53	± 28	(11)	71	± 24	(15)
1,1,1-Trichloroethane	48	± 29	(3)	98	± 45	(15)
1,1,2-Trichloroethane	67	± 32	(10)	86	± 21	(24)
Trichloroethene	42	± 28	(5)	71	± 26	(9)
Trichlorofluoromethane		—			—	
1,2,3-Trichloropropane		—		89	± 15	(5)
1,2,4-Trimethylbenzene	39		(1)	84	± 17	(8)
1,3,5-Trimethylbenzene		—			—	
Vinyl acetate	48	± 43	(5)	68		(2)
Mixed xylenes (total)	35		(1)	80	± 19	(5)

3. Collection and Storage of Samples

3.1. Ottawa sand is used as a blank soil matrix.

3.2. The QC spiking solution is refrigerated pending use. The maximum holding time for the analysis of volatile of organics on soil is 14 days.

4. Apparatus

4.1. Volumetric flasks: 5-mL, class A, glass.

4.2. Syringes: gas-tight, 10-, 25-, 50-, 100-, and 2500-μL.

4.3. Microspatula.

4.4. Pipettes: Pasteur, disposable, glass.

4.5. Pipette bulb: rubber, to fit Pasteur pipette.

4.6. Vials: 1.5-mL, glass, amber.

4.7. Caps: open-top, to fit vials.

4.8. Septa: Teflon/silicone discs to fit open-top caps.

4.9. Teflon tape.

4.10. Autosampler vials with Teflon-lined septa and crimp-tops: 11- x 30-mm vials and 11-mm silicone cap liner with Teflon face.

4.11. Portable crimper for sealing caps on autosampler vials.

4.12. Decapper for removing caps from autosampler vials.

4.13. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.14. Laboratory oven: capable of sustaining 100-150°C.

4.15. Labels printed with QC sample numbers.

5. Reagents

5.1. Methanol (reagent-grade).

5.2. Ottawa sand: a clean, dry 5.0-g aliquot is required for each sample.

5.2.1. Standard quality Ottawa sand, graded to 20-30 mesh and used for preparing cement tensile-strength samples, meets ASTM C190 specifications.

5.2.2. Ottawa sand heated to nominally 500°C for a minimum of 2 h is used as a sample matrix.

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade volatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem

Service, Inc., Box 3108, West Chester, PA 19381). Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8-12 mg of a solid volatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each solid analyte.

6.1.2. Add approximately 3 mL of methanol to the flask, stopper the flask, and swirl it to dissolve the analytes.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8-12 mg in 5 mL of stock solution. See Step 8.1.

6.1.5. Using a gas-tight syringe, add a liquid analyte just above the surface of the methanol. Stopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte added.

6.1.6. Dilute the solution to volume with methanol.

6.1.7. Mix by gently inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.1.8. Discard the solution in the neck of the flask to minimize concentration changes due to loss of volatile analytes from the surface of the solution.

6.1.9. The concentration of analytes in the stock solution will be between 1.5 - 2.5 mg/mL.

6.1.10. Transfer the stock solution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.11. Label the vials with information identifying the standard and with the expiration date.

6.1.12. The stock solution is stable for approximately 3 months when stored at -20°C.

6.2. Prepare additional stock solutions using different analytes chosen primarily from Table I. The number of analytes in the QC samples may be increased by using more than one stock solution to prepare the QC spiking solution.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100-150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with volatile analytes.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5-10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Sample size and container type may be varied to meet analytical requirements, avoiding the use of plastic containers for QC samples to be analyzed for organic constituents. This procedure describes the preparation of a volatiles on soil QC sample using 5 g of Ottawa sand.

7.3.2. Remove one or more vials of volatile stock standard from the freezer and allow them to reach room temperature. Do not allow the vials to sit at room temperature for longer than 2 h before preparing the QC spiking solution.

7.3.3. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.4. Using a gas-tight syringe, add 1500 μL of methanol to an autosampler vial to be used as a matrix for the QC spiking solution.

7.3.5. Seal the vial with a septum and crimp the top.

7.3.6. Spike a volume of stock standard, through the septum and below the surface of the methanol, to reach a concentration range of 75-150 μg/1.5 mL for each analyte in the QC spiking solution.

7.3.7. More than one stock standard may be spiked into the methanol to increase the number of analytes in the QC sample.

7.3.8. Replace the punctured septum and cap from the autosampler vial with a new septum and cap.

7.3.9. Label the vial with a QC sample number.

7.3.10. Include directions for the analyst to spike 10 μL of the QC spiking solution onto 5.0 g of preheated Ottawa sand just before analysis.

7.3.11. Return the stock standard to the freezer.

7.4. Refrigerate the QC spiking solution pending use. The maximum holding time for a volatile QC spiking solution for soil is 14 days.

7.5. The analyst will spike 10 μL of the QC spiking solution onto an accurately weighed 5.0-g aliquot of preheated Ottawa sand just before analysis.

7.6. Calculate the analyte concentrations in the QC sample in μg/kg based on a 10-μL aliquot of the QC spiking solution on 5.0000 g of preheated Ottawa sand.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the volume of neat liquid analyte needed to prepare a stock solution in the range of 8-12 mg/5 mL.

8.1.1. Read the density of the neat liquid analyte from Table I. The density of toluene is 0.867 mg/μL.

8.1.2. The desired weight spike range for 5 mL of stock solution is 8-12 mg of neat analyte.

8.1.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} = 9.2 \text{ to } 13.8\ \mu\text{L}$$

For toluene, between 9.2 and 13.8 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5 - 2.5 mg/mL in the stock solution.

8.2. Calculate the concentration of each analyte in the stock solution as in the following example.

8.2.1. If 12 μL of toluene, weighing 10.4 mg, is diluted in 5 mL of stock solution, the concentration of toluene in the stock solution is 2.08 mg/mL.

$$\frac{10.4 \text{ mg}}{5 \text{ mL}} = 2.08 \text{ mg/mL}$$

8.3. Calculate the concentration of each analyte in the QC spiking solution as in the following example.

8.3.1. The final volume of the QC spiking solution is the total of 1500 μL of methanol plus the volumes of all the QC spiking solutions added to the methanol.

8.3.2. If 60 μL of a stock solution containing 2.08 mg/mL of toluene and 50 μL of a second QC stock solution are both added to 1500 μL of methanol in an autosampler vial, the concentration of toluene in the QC spiking solution is 0.0775 μg/μL.

$$\frac{(2.08 \text{ mg/mL}) \left(\frac{1 \text{ mL}}{1000 \ \mu\text{L}}\right) (60 \ \mu\text{L}) \left(\frac{1000 \ \mu\text{g}}{1 \text{ mg}}\right)}{1500 \ \mu\text{L} + 60 \ \mu\text{L} + 50 \ \mu\text{L}} = 0.0775 \ \frac{\mu\text{g}}{\mu\text{L}}$$

8.4. Calculate the concentration of each analyte in the QC sample as in the following example.

8.4.1. When the analyst spikes 10 μL of the QC spiking solution containing 0.0775 μg/μL toluene onto 5.0000 g of preheated Ottawa sand, the concentration of toluene in the resulting QC sample will be 155 μg/kg. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(0.0775\ \mu g/\mu L)\ (10\ \mu L)}{(5.0000\ g)\ (kg/1000\ g)} = 155\ \mu g/kg$$

8.5. Record the analyte concentrations in the QC sample in μg/kg based on the analyst spiking a 10-μL aliquot of the QC spiking solution on 5.0000 g of preheated Ottawa sand.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form (WPF) number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Services (CST-17).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full, and keep the can in the secondary containment tray pending pickup by CST-17.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full, and keep the jar in the secondary containment tray pending pickup by CST-17.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-17 to pick up a full bag, can, or jar of waste contaminated with organic compounds using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2. CST-17 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.4 M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1993).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TABLE I. VOLATILE ORGANIC COMPOUNDS

Compound	CAS Number	Density of liquids (mg/μL)
acetone	67641	0.791
benzene	71432	0.874
bromobenzene	108861	1.491
bromochloromethane	74975	1.991
bromodichloromethane	75274	1.980
bromoform	75252	2.894
bromomethane	74839	0.838
2-butanone (MEK)	78933	0.805
n-butylbenzene	104518	0.860
sec-butylbenzene	135988	0.863
tert-butylbenzene	98066	0.867
carbon disulfide	75150	1.266
carbon tetrachloride	56235	1.594
chlorobenzene	108907	1.107
chlorodibromomethane	124481	2.451
chloroethane	75003	0.891
chloroform	67663	1.492
chloromethane	74873	gas
2-chlorotoluene	95498	1.083
4-chlorotoluene	106434	1.070
1,2-dibromo-3-chloropropane	96128	2.093
1,2-dibromoethane	106934	2.180
dibromomethane	74953	2.477
1,2-dichlorobenzene	95501	1.306
1,3-dichlorobenzene	541731	1.288
1,4-dichlorobenzene	106467	1.241
dichlorodifluoromethane	75718	gas
1,1-dichloroethane	75343	1.176
1,2-dichloroethane	107062	1.256
1,1-dichloroethene	75354	1.213
cis-1,2-dichloroethene	156592	1.284
trans-1,2-dichloroethene	156605	1.257
1,2-dichloropropane	78875	1.156
1,3-dichloropropane	142289	1.190
2,2-dichloropropane	594207	1.082
1,1-dichloropropene	563586	1.169
cis-1,3-dichloropropene	10061015	1.224
trans-1,3-dichloropropene	10061026	1.224
ethylbenzene	100414	0.867

TABLE I. VOLATILE ORGANIC COMPOUNDS (cont)

Compound	CAS Number	Density of liquids (mg/μL)
2-hexanone	591786	0.812
isopropylbenzene	98828	0.864
4-isopropyltoluene	99876	0.860
methylene chloride	75092	1.325
methyl iodide	74884	2.280
4-methyl-2-pentanone (MIK)	108101	0.800
n-propylbenzene	103651	0.862
styrene	100425	0.909
1,1,1,2-tetrachloroethane	630206	1.598
1,1,2,2,-tetrachloroethane	79345	1.586
tetrachloroethene	127184	1.623
toluene	108883	0.867
1,1,1-trichloroethane	71556	1.338
1,1,2-trichloroethane	79005	1.435
trichloroethene	79016	1.464
trichlorofluoromethane	75694	1.494
1,2,3-trichloropropane	96184	1.387
1,1,2-trichlorotrifluoroethane	76131	1.575
1,2,4-trimethylbenzene	95636	0.889
1,3,5-trimethylbenzene	108678	0.864
vinyl chloride	75014	0.9121
mixed xylenes (total)	1330207	0.860

VOLATILE ORGANIC COMPOUNDS IN WATER—QC SAMPLE PREPARATION

Analyte: Volatile organic compounds	**Method No.:** QCO260
Matrix: Water	**Range:** 30-150 μg/L
Procedure: Analysis by purge-and-trap extraction, gas chromatography and mass spectrometry (PTGC)	**Accuracy and Precision:** 100% ± 5.3% RSD
Effective Date: 04/25/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Material 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Prepare a stock solution in methanol of 3-6 volatile organic compounds chosen primarily from the list in Table I, found at the end of this procedure.

1.2. Prepare a 1:20 dilution in methanol of the stock solution.

1.3. Spike the diluted standard into distilled water.

2. Accuracy and Precision

2.1. The propagated error on quality control (QC) sample preparation is based on the error of the standard and on the error associated with the use of the microsyringe, balance, and volumetric flask. A relative standard deviation (RSD) of 5.3% at the 1-σ level has been calculated for standard preparation and for weighing, spiking, and dilution based on the following:

$$D = \frac{M1 \times M2 \times M4 \times M6}{M3 \times M5 \times M7} ,$$

where D = calculated result,
M1 = standard error,
M2 = weighing error,
M3 = first dilution error,
M4 = first pipette error,
M5 = second dilution error,

M6 = second pipette error, and
M7 = third dilution error.

2.1.1. Calculate relative variance for each variable using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3} + R^2_{M4} + R^2_{M5} + R^2_{M6} + R^2_{M7}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of balance,
R^2_{M3} = relative variance of first volumetric flask,
R^2_{M4} = relative variance of first microsyringe,
R^2_{M5} = relative variance of second volumetric flask,
R^2_{M6} = relative variance of second microsyringe,
R^2_{M7} = relative variance of third volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1990 and 1991 using this procedure and analyzed by purge-and-trap extraction, gas chromatography, and mass spectrometry are summarized and in Table II below. The data are published in Source Materials 10.1 to 10.3.

TABLE II. VOLATILE ORGANIC COMPOUNDS IN WATER SPIKE RECOVERY DATA

Compound	1990 Mean	±	std dev	(n)	1991 Mean	±	std dev	(n)
Acetone	—				95	±	8	(17)
Benzene	94	±	30	(13)	88			(1)
Bromobenzene	—				98	±	6	(9)
Bromochloromethane	110			(10)	—			
Bromodichloromethane	—				131			(2)
Bromoform	61			(1)	102	±	8	(8)
Bromomethane	—				—			
2-Butanone (MEK)	90	±	58	(19)	56	±	20	(3)
n-Butylbenzene	—				—			
sec-Butylbenzene	—				—			
tert-Butylbenzene	—				—			
Carbon disulfide	98	±	62	(14)	75	±	27	(4)
Carbon tetrachloride	76	±	12	(8)	89	±	22	(3)
Chlorobenzene	85	±	18	(20)	85	±	5	(10)
Chlorodibromomethane	82	±	22	(10)	95	±	15	(9)
Chloroethane	—				—			
Chloroform	—				100	±	13	(3)
2-Chlorotoluene	—				78	±	12	(4)
4-Chlorotoluene	—				—			
1,2-Dibromo-3-chloropropane	—				—			
1,2-Dibromoethane	108			(1)	—			
Dibromomethane	—				106	±	11	(3)
1,2-Dichlorobenzene	—				74			(2)
1,3-Dichlorobenzene	—				—			
1,4-Dichlorobenzene	64			(2)	—			
1,1-Dichloroethane	104	±	27	(22)	85	±	10	(4)
1,2-Dichloroethane	102	±	14	(16)	120	±	36	(9)
1,1-Dichloroethene	—				—			
cis-1,2-Dichloroethene	—				—			
trans-1,2-Dichloroethene	—				—			
1,2-Dichloropropane	96	±	20	(3)	86	±	13	(10)
1,3-Dichloropropane	—				—			
2,2-Dichloropropane	—				—			
1,1-Dichloropropene	—				—			
cis-1,3-Dichloropropene	52	±	10	(13)	—			
trans-1,3-Dichloropropene	169	±	35	(13)	—			
Ethylbenzene	78	±	18	(22)	75	±	10	(10)
2-Hexanone	94	±	43	(23)	72	±	32	(8)

TABLE II. VOLATILE ORGANIC COMPOUNDS IN WATER SPIKE RECOVERY DATA (cont)

Compound	1990 Mean	±	std dev	(n)	1991 Mean	±	std dev	(n)
Isopropylbenzene		—				—		
p-Isopropyltoluene		—				—		
Methylene chloride		—			80	±	23	(14)
4-Methyl-2-pentanone (MIK)		—			84	±	12	(5)
n-Propylbenzene		—			53	±	16	(4)
Styrene	77			(2)	67	±	19	(5)
1,1,1,2-Tetrachloroethane	97			(2)	87	±	5	(4)
1,1,2,2-Tetrachloroethane		—				—		
Tetrachloroethene	77	±	19	(19)	74	±	7	(9)
Toluene	80	±	19	(20)	75	±	4	(9)
1,1,1-Trichloroethane	85	±	24	(11)	86	±	16	(6)
1,1,2-Trichloroethane	94	±	10	(19)	95	±	8	(17)
Trichloroethene	76	±	9	(7)	82	±	5	(4)
Trichlorofluoromethane		—				—		
1,2,3-Trichloropropane		—			106	±	5	(4)
1,2,4-Trimethylbenzene		—			48	±	27	(3)
1,3,5-Trimethylbenzene		—				—		
Vinyl acetate	56	±	40	(8)		—		
Mixed xylenes	326			(1)	63	±	16	(4)

3. Collection and Storage of Samples

3.1. Distilled water purged with nitrogen gas is used as the blank matrix for spiking. Use water that has not been stored in plastic holding vessels or run through plastic tubing because phthalates may leach from plastics and contaminate the sample.

3.2. Spiked QC samples are refrigerated pending analysis. The maximum holding time for volatile organic compounds in water QC samples is 7 days. Preservation with HCl increases the holding time to 14 days.

4. Apparatus

4.1. Volumetric flasks: 5- and 50-mL, class A, glass.

4.2. Autopipette: 1000-μL, Rainin, or equivalent.

4.3. Pipette tips: disposable.

4.4. Syringes: gas-tight, 10-, 25-, 50-, 100-, and 500-μL.

4.5. Microspatula.

4.6. Pipettes: Pasteur, disposable, glass.

4.7. Pipette bulb: rubber, to fit Pasteur pipette.

4.8. Vials: 1.5-mL, glass, amber.

4.9. Caps: open-top, to fit vials.

4.10. Septa: Teflon/silicone discs to fit open-top caps.

4.11. Teflon tape.

4.12. Vials: 40-mL, zero headspace, with open-top screw caps with Teflon/silicone septa, pre-cleaned.

4.13. Analytical balance: 100-g minimum capacity, 0.1-mg accuracy.

4.14. Laboratory oven: capable of sustaining 100-150°C.

4.15. Bottle: gas-washing, with fritted dispersion disc, 500-mL minimum capacity.

4.16. Tubing and adapters: Teflon, to connect gas-washing bottle to nitrogen gas cylinder.

4.17. Labels printed with QC sample numbers.

5. Reagents

5.1. Methanol (analytical-grade).

5.2. Hydrochloric acid (concentrated, reagent-grade).

5.3. Nitrogen gas (high-purity) in a compressed gas cylinder.

6. Calibration and Standards

6.1. Prepare a stock solution of neat, standard-grade volatile analytes chosen primarily from Table I. Use Chem Service or equivalent chemicals (Chem Service, Inc., Box 3108, West Chester, PA 19381). Add solid analytes first, then liquid analytes after the addition of solvent.

6.1.1. Add 8-12 mg of a solid volatile analyte to a clean, tared 5.0-mL volumetric flask. Record the mass and tare the balance. Repeat for each analyte.

6.1.2. Add approximately 3 mL of methanol to the flask, stopper the flask, and swirl it to dissolve the analytes.

6.1.3. Place the stoppered flask on the analytical balance and tare the balance.

6.1.4. Calculate the volumes of liquid analytes needed to reach a weight spike range of 8-12 mg in 5 mL of stock solution. See Step 8.1.

6.1.5. Using a syringe, add a liquid analyte just above the surface of the methanol. Stopper the flask and record the mass and volume of the analyte added. Tare the balance. Repeat for each liquid analyte added.

6.1.6. Dilute the solution to volume with methanol.

6.1.7. Mix by **gently** inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.1.8. Discard the solution in the neck of the flask to minimize concentration changes due to loss of volatile analytes from the surface of the solution.

6.1.9. The concentration of analytes in the stock solution will be 1.5 - 2.5 mg/mL.

6.1.10. Transfer the stock solution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the caps.

6.1.11. Label the vials with information identifying the standard and with the expiration date.

6.1.12. The stock solution is stable for approximately 3 months when stored at -20°C.

6.2. Prepare additional stock solutions using different analytes chosen primarily from Table I. The number of analytes in the QC samples may be increased by combining the stocks in a 1:20 dilution.

6.3. Prepare a 1:20 dilution of the stock solution.

6.3.1. Add approximately 4 mL of methanol to a clean 5-mL volumetric flask.

6.3.2. Using a syringe, add 250 μL of a stock solution just above the surface of the methanol. Repeat for each stock solution to be combined in the 1:20 dilution.

6.3.3. Dilute the solution to volume with methanol.

6.3.4. Mix by gently inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

6.3.5. Discard the solution in the neck of the flask to minimize concentration changes due to the loss of volatile analytes from the surface of the solution.

6.3.6. The concentration of analytes in the dilution will be 0.075-0.125 mg/mL.

6.3.7. Transfer the dilution to 1.5-mL amber vials fitted with Teflon septa and caps. Wrap Teflon tape over and around the cap.

6.3.8. Label the vials with information identifying the standard and with the expiration date.

6.3.9. The standard dilution is stable for approximately 3 months when stored at -20°C.

7. Procedure

7.1. Cleaning glassware.

7.1.1. Wash volumetric flasks with detergent and rinse with hot tap water and then with methanol.

7.1.2. Store the glassware in a laboratory oven maintained at 100-150°C to minimize contamination.

7.2. Cleaning syringes.

7.2.1. Dedicate a group of syringes for use only with volatile analytes.

7.2.2. Fill the syringe through the needle with methanol. Discard the methanol into a waste container. Repeat for a total of 5-10 times.

7.2.3. Dry the syringe by pulling a vacuum on it for at least 10 min.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed.

7.3.1. Remove a vial of a 1:20 dilution of volatile stock standards from the freezer and allow it to reach room temperature. Do not let the vial sit at room temperature for longer than 2 h before spiking the QC sample.

7.3.2. Some analytes may crystallize out of solution in the freezer. Visually inspect the stock solution. If any precipitate is present, gently warm the solution on a hot plate and swirl it to redissolve the precipitate. Avoid excessive or prolonged heating, which would cause analytes to be lost from the solution.

7.3.3. Put 100-200 mL of distilled water into a gas-washing bottle fitted with a fritted gas-dispersion disc and connected to a nitrogen purge-gas tank. Use only distilled water that has not been stored in plastic or run through plastic tubing. Purge the water with nitrogen gas for at least 15 min to remove any volatile compounds dissolved in the water.

7.3.4. Add approximately 45 mL of the purged water to the 50-mL volumetric flask. Add 0.5 mL of concentrated HCl to the water as a preservative for the QC sample.

7.3.5. Spike a volume of a 1:20 dilution of a standard below the surface of the water to reach the desired spike range. Spike near the bottom of the flask using a syringe.

7.3.6 Dilute the solution to volume with purged water.

7.3.7. Mix by **gently** inverting three times.

NOTE: Vigorous shaking will cause the loss of volatile analytes.

7.3.8. Discard the solution in the neck of the flask to minimize concentration changes due to the loss of volatile analytes from the surface of the solution.

7.3.9. Pour the sample into a 40-mL, glass, zero-headspace vial leaving zero headspace. Discard the excess sample.

7.3.10. Label the vial with a QC sample number.

7.3.11. Return the 1:20 dilution of the standard to the freezer.

7.3.12. Refrigerate the QC sample pending analysis. The maximum holding time for volatile organic compounds in water QC samples preserved with HCl is 14 days.

7.4. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and enter them into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the volume of neat liquid analyte needed to prepare a stock solution in the range of 8-12 mg/5 mL.

8.1.1. Read the density of the neat liquid analyte from Table I. The density of toluene is 0.867 mg/μL.

8.1.2. The desired weight spike range for 5 mL of stock solution is 8-12 mg of neat analyte.

8.1.3. Divide the weight spike range by the density of the neat analyte to determine the desired volume spike range of neat analyte to use in 5 mL of stock solution.

$$\frac{8\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} \text{ to } \frac{12\ \text{mg}}{0.867\ \text{mg}/\mu\text{L}} = 9.2 \text{ to } 13.8\ \mu\text{L}$$

For toluene, between 9.2 and 13.8 μL of the neat analyte should be diluted to 5 mL to reach the desired concentration range of 1.5 - 2.5 mg/mL in the stock solution.

8.2. Calculate the concentration of each analyte in the stock solution as in the following example.

8.2.1. If 12 μL of toluene, weighing 10.4 mg, is diluted to 5 mL of stock solution, the concentration of toluene in the stock solution is 2.08 mg/mL.

$$\frac{10.4\ \text{mg}}{5\ \text{mL}} = 2.08\ \text{mg/mL}$$

8.3. Calculate the concentration of each analyte in the 1:20 dilution of the stock solution as in the following example.

8.3.1. If 250 μL of a stock solution containing 2.08 mg/mL of toluene is diluted to 5 mL with methanol, the concentration of toluene in the 1:20 stock dilution is 0.104 μg/μL.

$$\frac{(2.08\ \text{mg/mL})\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)(250\ \mu\text{L})}{(5\ \text{mL})\left(\frac{1000\ \mu\text{L}}{1\ \text{mL}}\right)} = 0.104\ \mu\text{g}/\mu\text{L}$$

8.4. Calculate the concentration of each analyte in the QC water sample as in the following example.

8.4.1. If 30 μL of a 1:20 stock dilution containing 0.104 μg/μL of toluene is spiked into 50 mL of distilled water, the concentration of toluene in the sample is 62 μg/L. Multiply the result by the RSD calculated in Step 2.1. to obtain the uncertainty.

$$\frac{(0.104\ \mu\text{g}/\mu\text{L})\ (30\ \mu\text{L})}{(50\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 62\ \mu\text{g/L}$$

8.5. Record the analyte concentration in the QC sample in μg/L.

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate solid waste (such as paper wipes, glass or plastic pipettes, empty vials, and incorrectly spiked QC samples contaminated with organic compounds) in a covered metal can lined with a plastic bag. Keep this segregated from PCB-contaminated solid waste and solid waste that is not contaminated with organic compounds.

9.1.2. Label the can with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as waste contaminated with organic compounds.

9.1.5. Place a new plastic bag into the waste can for continued use.

9.1.6. Accumulate the sealed bags in a larger container lined with a plastic bag and approved for the storage and transport of waste contaminated with organic compounds.

9.1.7. Identify the sealed bag with the current Waste Profile Form number describing the waste in the bag.

9.1.8. Label the larger container with a hazardous waste label and a label indicating its use for waste contaminated with organic compounds.

9.1.9. The larger container has a sealing cover. Open the can only for the time necessary to add waste.

9.1.10. When the plastic bag liner is full, seal it with tape and keep it in the sealed container pending pickup by Waste Management (CST-7).

9.2. Liquid waste.

9.2.1. Liquid waste containing organic compounds (such as rinses from syringes, excess QC samples, and incorrectly spiked QC samples) is accumulated in a covered metal can in a secondary containment tray.

9.2.1.1. Liquid waste containing organic compounds but no PCBs is kept segregated from PCB-contaminated liquid waste.

9.2.1.2. Label the can with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.1.3. Cap the can when full, and keep the can in the secondary containment tray pending pickup by CST-7.

9.2.1.4. Label a new can for future use.

9.2.2. Accumulate 2-mL vials containing out-of-date spiking solutions of organic compounds in a glass jar in a secondary containment tray.

9.2.2.1. Keep solutions that are not contaminated with PCBs segregated from those that are PCB-contaminated.

9.2.2.2. Label the jar with a hazardous waste label and a label indicating its use for waste containing organic compounds.

9.2.2.3. Open the jar only for the period of time necessary to add vials.

9.2.2.4 Cap the jar when full, and keep the jar in the secondary containment tray pending pickup by CST-7.

9.2.2.5. Label a new jar for future use.

9.3. Waste pickup.

9.3.1. Request CST-7 to pick up a full bag, can, or jar of waste contaminated with organic compounds using the current Chemical Waste Disposal Request (CWDR) form. The current Waste Profile Form that describes the waste is referenced on the CWDR.

9.3.2. CST-7 picks up the waste for disposal according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TABLE I. VOLATILE ORGANIC COMPOUNDS

Compound	CAS Number	Density of liquids (mg/μL)
acetone	67641	0.791
benzene	71432	0.874
bromobenzene	108861	1.491
bromochloromethane	74975	1.991
bromodichloromethane	75274	1.980
bromoform	75252	2.894
bromomethane	74839	0.838
2-butanone (MEK)	78933	0.805
n-butylbenzene	104518	0.860
sec-butylbenzene	135988	0.863
tert-butylbenzene	98066	0.867
carbon disulfide	75150	1.266
carbon tetrachloride	56235	1.594
chlorobenzene	108907	1.107
chlorodibromomethane	124481	2.451
chloroethane	75003	0.891
chloroform	67663	1.492
chloromethane	74873	gas
2-chlorotoluene	95498	1.083
4-chlorotoluene	106434	1.070
1,2-dibromo-3-chloropropane	96128	2.093
1,2-dibromoethane	106934	2.180
dibromomethane	74953	2.477
1,2-dichlorobenzene	95501	1.306
1,3-dichlorobenzene	541731	1.288
1,4-dichlorobenzene	106467	1.241
dichlorodifluoromethane	75718	gas
1,1-dichloroethane	75343	1.176
1,2-dichloroethane	107062	1.256
1,1-dichloroethene	75354	1.213
cis-1,2-dichloroethene	156592	1.284
trans-1,2-dichloroethene	156605	1.257
1,2-dichloropropane	78875	1.156
1,3-dichloropropane	142289	1.190
2,2-dichloropropane	594207	1.082
1,1-dichloropropene	563586	1.169
cis-1,3-dichloropropene	10061015	1.224
trans-1,3-dichloropropene	10061026	1.224
ethylbenzene	100414	0.867

TABLE I. VOLATILE ORGANIC COMPOUNDS (cont)

Compound	CAS Number	Density of liquids (mg/μL)
2-hexanone	591786	0.812
isopropylbenzene	98828	0.864
4-isopropyltoluene	99876	0.860
methylene chloride	75092	1.325
methyl iodide	74884	2.280
4-methyl-2-pentanone (MIK)	108101	0.800
n-propylbenzene	103651	0.862
styrene	100425	0.909
1,1,1,2-tetrachloroethane	630206	1.598
1,1,2,2,-tetrachloroethane	79345	1.586
tetrachloroethene	127184	1.623
toluene	108883	0.867
1,1,1-trichloroethane	71556	1.338
1,1,2-trichloroethane	79005	1.435
trichloroethene	79016	1.464
trichlorofluoromethane	75694	1.494
1,2,3-trichloropropane	96184	1.387
1,1,2-trichlorotrifluoroethane	76131	1.575
1,2,4-trimethylbenzene	95636	0.889
1,3,5-trimethylbenzene	108678	0.864
vinyl chloride	75014	0.9121
mixed xylenes (total)	1330207	0.860

AMERICIUM-241 IN URINE — QC SAMPLE PREPARATION

Analyte: Americium-241	**Method No.:** QCR100
Matrix: Urine	**Spike Range:** 0.0 to 1.0 pCi/sample
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 4% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.11 to 10.13 for proper waste disposal practices.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 4.0% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2},$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{\frac{\left[R^2_{M1} (M_3 + M_2)^2 + M_3^2 (R^2_{M2} + R^2_{M3})\right]}{(M_3 + M_2)^2}} \times 100 ,$$

where S_{D_T} = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
M_3 = volume of cylinder,
M_2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2. Analysis by radiochemistry and alpha spectrometry of QC samples prepared between 1986 and 1989 using this procedure gave a mean recovery of 102% ± 3% RSD. The data are published in Source Materials 10.1 through 10.6 and are summarized in Table I below.

TABLE I. AMERICIUM-241 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR AMERICIUM-243 RECOVERY

Year	Spike level pCi/sample	Mean ± RSD (%)	Number of samples
1986	0.23	114 ± 3	3
	0.46	100 -	1
	0.55	100 -	1

TABLE I. AMERICIUM-241 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR AMERICIUM-243 RECOVERY (cont)

Year	Spike level pCi/sample	Mean ± RSD (%)	Number of samples
1987	0.23	104 -	1
1987	0.54	112 ± 3	2
	0.90	109 ± 3	2
1988	0.24	104 -	1
	0.48	88 -	1
	0.58	97 -	1
	0.96	104 -	1
1989	0.24	92 ± -	1
	0.48	96 ± -	1
	0.96	102 ± -	2

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work and is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 500-mL.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 16-oz jars with screw caps.

4.6. Labels printed with QC sample numbers.

4.7. Heat lamp.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with an ^{241}Am standard prepared in 4 N HNO_3. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.2. The ^{241}Am standard should be at a concentration of approximately 1.0 pCi/mL.

6.3. The ^{241}Am standard was calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NIST SRM 4322. Recalibrate the standard solution yearly by direct plating and alpha scintillation counting. Record all data in the QC laboratory notebook.

6.4. Direct plating procedure.

6.4.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, then evaporate to dryness under a heat lamp.

6.4.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper assures a tightly sealed package when assembled.

6.4.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.4.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.4.5. Place a piece of Mylar film over all the layers.

6.4.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.4.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.4.8. The count room data are corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates, then assign the value to the standard.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Remove gloves, discard them in the biohazard waste container, and wash hands with soap and water.

7.2. Prepare a pool from blank urine sufficient in volume to allow 400 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples.

7.4. Record QC standard information, sample spike amount, concentration, and uncertainty in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 400 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentrations of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Record spike concentrations as pCi/sample of urine.

8.2. Calculate the spike concentration for a 500-μL aliquot of ^{241}Am standard using the following equation:

$$\text{pCi/sample per spike amount} = (1.0\ \text{pCi/mL}) \times 0.500\ \text{mL} = 0.50\ \text{pCi/sample} \quad .$$

8.3. Spike concentrations calculated in Step 8.2 are tabulated below.

Spike amount (μL)	Concentration (pCi/sample)	Uncertainty (±4.0%)
250	0.25	0.01
500	0.50	0.02
600	0.60	0.02
900	0.90	0.04

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. Dispose of bottles used to collect blank urine for a QC sample matrix as uncontaminated laboratory trash after they have been rinsed with dilute bleach solution.

9.2.2.2. Accumulate solid waste (such as paper wipes, plastic pipettes, and rubber gloves contaminated with biohazardous material, primarily urine) in a plastic bag labeled for the collection of biohazardous waste and keep it segregated from waste with no biohazard contamination.

9.2.2.3. Transfer full bags of biohazardous waste to a cardboard box labeled with a biohazard label and lined with a plastic bag bearing a biohazard label.

9.2.2.4. When the cardboard box is full, seal the liner bag and the box.

9.2.2.5. Line a new biohazard waste box with a plastic bag for further use.

9.3. Waste pickup.

9.3.1. Radiochemically contaminated waste.

9.3.1.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.1.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.2. Biohazardous waste.

9.3.2.1. Request CST-7 to pick up a full box of biohazardous waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2.2. CST-7 arranges for pickup and disposal of the waste by the company currently under contract with the Laboratory for that purpose.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

10.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

10.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

10.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

10.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

10.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.7. *EML Procedures Manual*, 25th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.8. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4322, Americium-241 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, November 1986).

10.9. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard," (National Institute of Standards and Technology, Washington, DC, April 1982).

10.10. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.11. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.12. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.13. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

CESIUM-137 ON SOIL — QC SAMPLE PREPARATION

Analyte: Cesium-137	**Method No.:** QCR110
Matrix: Sand	**Spike Range:** 5 to 60 pCi/g
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 04/12/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with a ^{137}Cs standard. The sand is used in place of soil as the quality control (QC) matrix for ^{137}Cs analysis by gamma-ray spectrometry.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC samples can be reused provided the ^{137}Cs concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared during 1991 and 1992 using this procedure gave a mean recovery of 99% ± 26% at the 1-σ level. The data are published in Source Material 10.1 and 10.2 and are summarized below.

TABLE I. CESIUM-137 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

	Spike range pCi/g	Mean ± RSD (%)	Number of samples
1991	0 to 15	105 ± 8	7
	15 to 30	109 ± 9	3
1992	0 to 15	112 ± 17	13
	15 to 30	122 ± 12	8
	30 to 45	121 ± 19	4
	45 to 70	120 ± 22	2

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g minimum capacity, 0.1-g accuracy.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Heat lamp.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. Sand. A clean and dry 100-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standard should be calibrated against a National Institute of Standards and Technology (NIST) - certified ^{137}Cs Standard Reference Material (SRM) solution such as NIST SRM 4233-B. The standard solution should be

recalibrated yearly using gamma spectroscopy. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$ or the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 100-g aliquot of the unspiked sand as a blank.

7.2. Accurately weigh 100 g of sand into a 500-mL high-density polyethylene bottle. Record the weight of the sand on the bottle for reference by the analyst.

7.3. Spike an aliquot of ^{137}Cs standard onto the sand to reach a ^{137}Cs concentration in the desired spike range. Be careful to wet only the sand and not the container walls.

7.4. Dry the spiked sand under a heat lamp. Periodically mix the sample by shaking it until all large clumps are broken up.

7.5. Cap the bottle and label it with a QC sample number.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{137}Cs on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 500 µL of a 6000-pCi/mL ^{137}Cs standard is used to spike 100.0 g of sand, the ^{137}Cs concentration in the sand will be 30 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(6000\ \text{pCi/mL})\ (500\ \mu\text{L})\ (1\ \text{mL}/1000\ \mu\text{L})}{100.0\ \text{g}} = 30\ \text{pCi/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste Pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, E. A. Jones, N. L. Koski, B. T. O'Malley, G. H. Brooks, W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2 M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (in preparation).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (National Institute of Standards and Technology, Washington, DC, November 1979).

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

CESIUM-137 ON VEGETATION ASH — QC SAMPLE PREPARATION

Analyte: Cesium-137	**Method No.:** QCR120
Matrix: Vegetation ash	**Spike Range:** 5 to 60 pCi/g
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 04/19/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Blank vegetation ash is spiked with a ^{137}Cs standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC sample can be reused provided the ^{137}Cs concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared between 1990 and 1992 using this procedure gave a mean recovery of 102% ± 38% at the 1-σ level (N = 11). The data are published in Source Materials 10.1 through 10.3.

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g minimum capacity, 0.1-g accuracy.

4.3. Spatula.

4.4. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.5. Pipette tips: disposable.

4.6. Heat lamps.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Blank vegetation ash is used as the sample matrix. A 100-g aliquot is required for each sample.

5.2. A suitable vegetation ash does not contain the analyte of interest and presents few interferences to the analytical method. Commercially available dry pet or farm stock foods may provide a suitable matrix.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{137}Cs Standard Reference Material (SRM) solution such as NIST SRM 4233-B. The standard solution should be recalibrated yearly using gamma spectroscopy. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} \quad ,$$

where A_t = the activity at desired time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$ or the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 100-g aliquot of the unspiked vegetation ash as a blank.

7.2. Accurately weigh 100 g of blank vegetation ash into a 500-mL high-density polyethylene bottle. Record the weight of ash on the bottle for reference by the analyst.

7.3. Pipette an aliquot of ^{137}Cs standard onto the ash to reach a ^{137}Cs concentration in the desired spike range. Be careful to wet only the ash and not the container walls.

7.4. Dry the spiked sample under a heat lamp, periodically mixing it by shaking, until completely dry and homogeneous.

7.5. Cap the bottle and label it with a QC sample number.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{137}Cs in the vegetation ash sample as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 750 µL of a 6000-pCi/mL ^{137}Cs standard is spiked on 100.0 g of blank vegetation ash, the concentration of ^{137}Cs in the ash will be 45 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(6000\ \text{pCi/mL})\ (750\ \mu\text{L})\ (1\ \text{mL}/1000\ \mu\text{L})}{100.0\ \text{g}} = 45\ \text{pCi/g}$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (in preparation).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (National Institute of Standards and Technology, Washington, DC, November 1979).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

CESIUM-137 IN WATER — QC SAMPLE PREPARATION

Analyte: Cesium-137	**Method No.:** QCR130
Matrix: Water	**Spike Range:** 500 to 2000 pCi/L
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 04/17/90	**Author:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Water is spiked with a ^{137}Cs standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.3. Because the method of analysis is nondestructive, the QC sample can be reused provided the ^{137}Cs concentration is decayed periodically.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared during 1991 and 1992 using this procedure gave a mean recovery of 91% ± 14% at the 1-σ level. The data are published in Source Material 10.1 and 10.2 and are summarized below.

TABLE I. CESIUM-137 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

	Spike range pCi/L	Mean ± std dev (%)	Number of samples
1991	500 to 1000	128 ± 16	4
	1000 to 2000	107 ± 1	3
1992	500 to 1000	106 ± 32	10
	1000 to 2000	90 ± 26	3

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flask: 500-mL, glass, class A.

4.2. Bottles: 500-mL, high-density polyethylene.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentrations.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standards should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{137}Cs Standard Reference Material (SRM) solution such as NIST SRM 4233-B. The standard solution should be recalibrated yearly using gamma spectroscopy. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} \quad ,$$

where A_t = the activity at desired time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$ or the decay constant where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 500-mL aliquot of the unspiked acidified water as a blank.

7.2. Measure approximately 400 mL of distilled water into a 500-mL volumetric flask.

7.3. Add 1.25 mL of concentrated HNO_3 to the water in the flask to reach a pH of approximately 1.

7.4. Spike an aliquot of ^{137}Cs standard into the flask to reach a ^{137}Cs concentration in the desired spike range.

7.5. Fill the volumetric flask to volume with distilled water and mix by inverting.

7.6. Transfer the solution to a 500-mL high-density polyethylene bottle, and label it with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{137}Cs in the solution as nCi/L or pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 100 µL of a 6000-pCi/mL ^{137}Cs standard is used to spike 500 mL of acidified water, the concentration of ^{137}Cs in the acidified water will be 1200 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(6000\ \text{pCi/mL})\ (100\ \mu\text{L})\ (1\ \text{mL}/1000\ \mu\text{L})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 1200\ \text{pCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, E. A. Jones, N. L. Koski, B. T. O'Malley, G. H. Brooks, W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (in preparation).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (National Institute of Standards and Technology, Washington, DC, November 1979).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

GROSS ALPHA AND GROSS BETA ON SOIL — QC SAMPLE PREPARATION

Analyte: Gross alpha and gross beta	**Method No.:** QCR140
Matrix: Sand	**Spike Range:** 2.5–10 pCi/g
Procedure: Proportional counting	**Accuracy and Precision:** Gross alpha 100% ± 4.5% RSD Gross beta 100% ± 3.2% RSD
Effective Date: 06/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand spiked with ^{241}Am and ^{90}Sr standards is used in place of soil as the quality control (QC) matrix for gross alpha and gross beta analysis by proportional counting.

1.2. Gross beta is contributed equally by ^{90}Sr and the ^{90}Y radioactive decay products that are in equilibrium in the ^{90}Sr standard solution.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 4.5% at the 1-σ level for gross alpha and 3.2% at the 1-σ level for gross beta has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1991 and 1993 using this procedure and analyzed by proportional counting are tabulated below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY FOR GROSS ALPHA AND GROSS BETA ON SOIL

	Gross Alpha		Gross Beta	
	Mean ± std dev (%)	N	Mean ± std dev (%)	N
1991	95 ± 44	8	93 ± 18	8
1992	123 ± 55	27	115 ± 24	27
1993	119 ± 28	8	120 ± 29	8

N = Number of samples.

3. Collection and Storage of Samples

3.1. Store QC samples in glass beakers covered with plastic wrap at room temperature pending analysis.

4. Apparatus

4.1. Beakers: 100-mL, glass.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Balance: 200-g minimum capacity, 0.1-mg accuracy.

4.5. Spatula.

4.6. Plastic wrap.

4.7. Heat lamp.

4.8. Labels printed with QC sample numbers.

4.9. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.10. Discs: stainless-steel, 2.22-cm-diam.

4.11. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.12. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.13. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Sand. A clean, dry 2-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. When certified primary standards are available, dilute them to make standards at the desired concentration.

6.2. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.3. Gross alpha.

6.3.1. Spike QC samples with an ^{241}Am standard prepared in 4 N HNO_3 at a concentration of approximately 180 pCi/mL. Count the solution on a zinc sulfide scintillation system calibrated with National Bureau of Standards (NBS) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.3.2. Calibrate the ^{241}Am standard against a National Institute of Standards (NIST)-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.3.3. Direct plating procedure.

6.3.3.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.3.3.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper assures the package is tightly sealed when assembled.

6.3.3.3. Place the stainless-steel disc containing the sample on the filter paper, making sure to center the disc.

6.3.3.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.3.3.5. Place a piece of Mylar film over all the layers.

6.3.3.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.3.3.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) count for each sample.

6.3.3.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.4. Gross beta.

6.4.1. Spike QC samples with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 180 pCi/mL.

6.4.2. Calibrate the ^{90}Sr standard against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.4.3. Decay the ^{90}Sr standards each year.

6.4.3.1. The half-life of ^{90}Sr is 28.5 years.

6.4.3.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 2-g sample aliquot in a 100-mL glass beaker.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 2-g aliquot of the deep-well sand for use as a blank, omitting the ^{241}Am, the ^{90}Sr, or both.

7.3. Accurately weigh a 2-g aliquot of clean, dry sand into a 100-mL beaker. Record the weight of the sand on the beaker with a felt-tipped pen for reference by the analyst.

7.4. Spike an aliquot of ^{241}Am standard onto the sand in the beaker to reach the desired spike range for gross alpha.

7.5. The gross beta count is contributed equally by ^{90}Sr and the ^{90}Y radioactive decay products, which are in equilibrium in the ^{90}Sr standard solution.

7.5.1. The concentration of the ^{90}Sr standard solution is expressed in terms of ^{90}Sr although half the gross beta count is contributed by ^{90}Sr and the other half by ^{90}Y.

7.5.2. Divide the spike range in half and use the concentration of the ^{90}Sr standard solution to determine the amount of standard solution to use to reach the desired spike range of 1.25–5.0 pCi/g.

7.5.3. Spike the determined amount of ^{90}Sr standard onto the sand in the beaker.

7.5.4. The gross beta count will be within the spike range of 2.5–10.0 pCi/g because ^{90}Y in the standard solution contributes a gross beta count equal to that contributed by the ^{90}Sr. The beta concentration in the QC sample based on the amount of ^{90}Sr added must be multiplied by 2 to determine the total gross beta concentration.

7.6. Label the beaker with a QC sample number.

7.7. Air dry the QC sample or dry it under a heat lamp to remove excess moisture.

7.8. Cover the beaker with plastic wrap and store the sample at room temperature pending analysis.

7.9. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Determine background contributions to gross alpha and gross beta counts and add them to the spiked alpha and beta concentrations.

8.2. Record the gross alpha and gross beta concentrations on the sand as pCi/g.

8.3. Calculate the gross alpha spike concentration as in the following example.

8.3.1. If 50 μL of a 180-pCi/mL ^{241}Am standard is spiked onto 2.0000 g of sand, the gross alpha concentration in the sand is 4.5 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(180\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (50\ \mu\text{L})}{2.0000\ \text{g}} = 4.5\ \text{pCi/g} \quad .$$

8.3.2. Add the alpha background to the alpha concentration from the ^{241}Am spike to obtain the total gross alpha concentration in the QC sample.

$$4.5\ \text{pCi/g} + 4.9\ \text{pCi/g} = 9.4\ \text{pCi/g} \quad .$$

8.4. Calculate the gross beta concentration as in the following example.

8.4.1. If 35 μL of a 174-pCi/mL ^{90}Sr standard is spiked onto 2.000 g of sand, the beta concentration contributed by ^{90}Sr in the sample is 3.0 pCi/g.

$$\frac{(174\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (35\ \mu\text{L})}{2.0000\ \text{g}} = 3.0\ \text{pCi/g} \quad .$$

8.4.2. Multiply the beta concentration contributed by ^{90}Sr by 2 to determine the combined gross beta concentration contributed by ^{90}Sr and ^{90}Y.

$$(3.0\ \text{pCi/g})\ (2) = 6.0\ \text{pCi/g} \quad .$$

8.4.3. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.4.4. Add the beta background to the beta concentration contributed by the combined ^{90}Sr and ^{90}Y to obtain the total gross beta concentration in the QC sample.

$$6.0 \text{ pCi/g} + 2.4 \text{ pCi/g} = 8.4 \text{ pCi/g} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, and G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.6. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

GROSS ALPHA AND GROSS BETA IN WATER — QC SAMPLE PREPARATION

Analyte: Gross alpha and gross beta	**Method No.:** QCR150
Matrix: Water	**Spike Range:** 5–20 pCi/L
Procedure: Proportional counting	**Accuracy and Precision:** Gross alpha 100% ± 3.4% RSD Gross beta 100% ± 3.2% RSD
Effective Date: 06/01/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of gross alpha and gross beta in water is prepared by spiking 0.5 M HCl with ^{241}Am and ^{90}Sr standards.

1.2. Gross beta is contributed equally by ^{90}Sr and by the ^{90}Y radioactive decay products that are in equilibrium in the ^{90}Sr standard solution.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the volumetric flask and of the pipette. A relative standard deviation (RSD) of 3.4% at the 1-σ level for gross alpha and 3.2% at the 1-σ level for gross beta has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2 Analytical results from QC samples prepared between 1991 and 1993 using this procedure and analyzed by proportional counting are summarized in Table I below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY FOR GROSS ALPHA AND GROSS BETA IN WATER

	Gross Alpha		Gross Beta	
	Mean ± std dev (%)	N	Mean ± std dev (%)	N
1991	130 ± 47	17	90 ± 32	15
1992	140 ± 29	25	110 ± 32	23
1993	115 ± 40	24	105 ± 20	28

N = Number of samples.

3. Collection and Storage of Samples

3.1. QC samples are prepared in an acid medium in a volumetric flask and stored in the flask at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 1-L, glass, class A.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Labels printed with QC sample numbers.

4.5. Heat lamp.

4.6. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.7. Discs: stainless-steel, 2.22-cm-diam.

4.8. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.9. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.10. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Numours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. When they are available, dilute certified primary standards to make standards at the desired concentration.

6.2. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.3. Gross alpha.

6.3.1. Spike QC samples with an ^{241}Am standard prepared in 4 N HNO_3 at a concentration of approximately 18 pCi/mL. Count the solution on a

zinc sulfide scintillation system calibrated with National Bureau of Standards (NBS) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.3.2. Calibrate the ^{241}Am standard against a National Institute of Standards and Technology (NIST)-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.3.3. Direct plating procedure.

6.3.3.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.3.3.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures the package is tightly sealed when assembled.

6.3.3.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.3.3.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.3.3.5. Place a piece of Mylar film over all the layers.

6.3.3.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.3.3.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) count for each sample.

6.3.3.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.4. Gross beta.

6.4.1. Spike QC samples with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 170 pCi/mL.

6.4.2. Calibrate the ^{90}Sr standard against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.4.3. Decay the ^{90}Sr standards each year.

6.4.3.1. The half-life of ^{90}Sr is 28.5 years.

6.4.3.2. The following equation describes the rate of radioactive decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 1-L sample aliquot in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically omit the ^{241}Am, the ^{90}Sr, or both from the QC sample for use as a blank.

7.3. Add approximately 800 mL of distilled water to a 1-L volumetric flask.

7.4. Add 43 mL of 12 M HCl to the water in the flask to produce a final acid concentration of 0.5 M.

7.5. Spike an aliquot of ^{241}Am standard into the water in the flask to reach the desired spike range for gross alpha.

7.6. The gross beta count is contributed equally by ^{90}Sr and by the ^{90}Y radioactive decay products that are in equilibrium in the ^{90}Sr standard solution.

7.6.1. The concentration of the ^{90}Sr standard solution is expressed in terms of ^{90}Sr although half the gross beta count is contributed by ^{90}Sr and the other half by ^{90}Y.

7.6.2. Divide the spike range in half and use the concentration of the ^{90}Sr standard solution to determine the amount of standard solution to use to reach the desired spike range of 2.5–10.0 pCi/L.

7.6.3. Spike the determined amount of ^{90}Sr standard into the water in the flask.

7.6.4. The gross beta count will be within the spike range of 5–20 pCi/L because ^{90}Y in the standard solution contributes a gross beta count equal to that contributed by the ^{90}Sr. The beta concentration in the QC sample based on the amount of ^{90}Sr added must be multiplied by 2 to determine the total gross beta concentration.

7.7. Dilute the QC sample to volume with distilled water. Mix by inversion. Label the flask with a QC sample number and store at room temperature pending analysis.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of gross alpha and gross beta in the QC sample as pCi/L.

8.2. Calculate the gross alpha spike concentration as in the following example.

8.2.1. If 300 μL of a 17.73-pCi/mL ^{241}Am standard is used to prepare a 1-L QC sample, the gross alpha concentration in the sample is 5.3 pCi/L.

$$\frac{(17.73\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (300\ \mu\text{L})}{1\ \text{L}} = 5.3\ \text{pCi/L} \quad .$$

8.2.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.3. Calculate the gross beta spike concentration as in the following example.

8.3.1. If 25 μL of a 174-pCi/mL ^{90}Sr standard is used to prepare a 1-L QC sample, the beta concentration contributed by ^{90}Sr in the sample is 4.4 pCi/L.

$$\frac{(174\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (25\mu\text{L})}{1\ \text{L}} = 4.4\ \text{pCi/L} \quad .$$

8.3.2. Multiply the beta concentration contributed by ^{90}Sr by 2 to determine the total gross beta concentration contributed by ^{90}Sr and ^{90}Y.

$$(4.4\ \text{pCi/L})\ (2) = 8.8\ \text{pCi/L} \quad .$$

8.3.3. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.6. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

GROSS GAMMA ON SOIL — QC SAMPLE PREPARATION

Analyte: Gross gamma	**Method No.:** QCR153
Matrix: Sand	**Spike Range:** 5–15 pCi/g
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 03/02/92 to 09/22/94	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1 Cesium-137 is used as a representative gamma emitter. To determine the gross gamma concentration of the quality control (QC) sample, use only the fraction of gamma radiation emitted at energy levels exceeding the lower energy threshold of the analytical method used to measure the quality control (QC) sample.

1.2. Sand is spiked with a gross gamma standard. The sand is used in place of soil as the QC matrix for gross gamma analysis by gamma-ray spectrometry.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.4. Because the method of analysis is nondestructive, the QC samples can be reused providing the gross gamma concentration is periodically decayed.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared during 1992 and 1993 using this procedure (N = 9) gave a mean recovery of 118% ± 39% at the 1-σ level.

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g minimum capacity, 0.1-g accuracy.

4.3. Spatula.

4.4. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.5. Pipette tips: disposable.

4.6. Heat lamp.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Sand. A clean, dry 100-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL. The gross gamma concentration of the standard is calculated from the ^{137}Cs concentration. See Step 8.1.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{137}Cs Standard Reference Material (SRM) solution, such as NIST SRM 4233-B, containing 19 μg of high-purity cesium chloride per gram in 1 M HCl. The standards should be recalibrated yearly using gamma spectrometry. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = the decay constant, (ln 2)/$T_{1/2}$, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 100-g aliquot of the unspiked sand as a blank.

7.2. Calculate the gross gamma concentration of the ^{137}Cs standard by multiplying the ^{137}Cs concentration by the fraction of the total gamma radiation emitted by ^{137}Cs at energy levels exceeding the lower energy threshold of the analytical method used to measure the QC samples. If the lower energy threshold is 100 keV, only 0.851 of the total gamma radiation emitted by ^{137}Cs is at a higher energy level (662 keV). See Step 8.1.

7.3. Accurately weigh 100 g of sand into a 500-mL, high-density polyethylene bottle. Record the weight of the sand on the bottle for reference by the analyst.

7.4. Spike an aliquot of gross gamma standard onto the sand to reach a gross gamma concentration in the desired spike range. Be careful to wet only the sand and not the container walls.

7.5. Dry the spiked sand under a heat lamp. Periodically mix the sample by shaking it until all large clumps are broken up and the sand is dry.

7.6. Cap the bottle and label it with a QC sample number.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the gross gamma concentration of a ^{137}Cs standard using the following example.

8.1.1. If the lower energy threshold of the analytical method used to measure the QC samples is 100 keV, only 0.851 of the gamma radiation emitted by ^{137}Cs is at an energy level (662 keV) exceeding the lower energy threshold and may be used to determine gross gamma concentration.

8.1.2. A standard with a ^{137}Cs concentration of 6000 pCi/mL has a gross gamma concentration with energy levels exceeding 100 keV of 5106 pCi/mL.

$$\left(\frac{6000\ \text{pCi}}{1\ \text{mL}}\right)(0.851) = 5106\ \text{pCi/mL}\ .$$

8.2. Calculate the gross gamma concentration of the QC sample as in the following example.

8.2.1. If 200 µL of a 5106-pCi/mL gross gamma standard is used to spike 100.0 g of sand, the gross gamma concentration in the sand will be 10.2 pCi/g.

$$\frac{\left(\frac{5106\ \text{pCi}}{1\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(200\mu\text{L})}{100.0\ \text{g}} = 10.2\ \text{pCi/g}\ .$$

8.2.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.2.3. Record the concentration of gross gamma in the QC sample as pCi/g.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-up Standard" (Washington, DC, November 1979).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

GROSS GAMMA IN WATER — QC SAMPLE PREPARATION

Analyte: Gross gamma	**Method No.:** QCR155
Matrix: Water	**Spike Range:** 1000–1500 pCi/L
Procedure: Gamma-ray spectrometry	**Accuracy and Precision:** 100% ± 3.3 RSD
Effective Date: 03/02/92 to 09/22/94	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.2 and 10.3 for proper waste disposal practices.

1. Principle of Method

1.1. Cesium-137 is used as a representative gamma emitter. To determine the gross gamma concentration of the quality control (QC) sample, use only the fraction of gamma radiation emitted at energy levels exceeding the lower energy threshold of the analytical method used to measure the QC sample.

1.2. Water is spiked with a gross gamma standard.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

1.4. Because the method of analysis is nondestructive, the QC sample can be reused providing the gross gamma concentration is periodically decayed.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by gamma-ray spectrometry of QC samples prepared during 1992 and 1993 using this procedure (N = 24) gave a mean recovery of 108% ± 16% at the 1-σ level.

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flask: 500-mL, glass, class A.

4.2. Bottles: 500-mL, high-density polyethylene.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Labels printed with QC sample numbers.

5. Reagents

5.1. Nitric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with a ^{137}Cs standard prepared in 1 M HCl at a concentration of approximately 6000 pCi/mL. The gross gamma concentration of the standard is calculated from the ^{137}Cs concentration. See Step 8.1.

6.2. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.3. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.4. The ^{137}Cs standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{137}Cs Standard Reference Material (SRM) solution, such as NIST SRM 4233-B, containing 19 μg of high-purity cesium chloride per gram in 1 M HCl. The standards should be recalibrated yearly using gamma spectrometry. Record all data in the QC Laboratory notebook.

6.5. Decay the ^{137}Cs standards each year.

6.5.1. The half-life of ^{137}Cs is 30 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} \quad ,$$

where A_t = the activity at desired time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = the decay constant, $(\ln 2)/T_{1/2}$, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 500-mL aliquot of the unspiked acidified water as a blank.

7.2. Calculate the gross gamma concentration of the ^{137}Cs standard by multiplying the ^{137}Cs concentration by the fraction of the total gamma radiation emitted by ^{137}Cs at energy levels exceeding the lower energy threshold of the analytical method used to measure the QC samples. If the lower energy threshold is 100 keV, only 0.851 of the total gamma radiation emitted by ^{137}Cs is at a higher energy level (662 keV). See Step 8.1.

7.3. Place approximately 400 mL of distilled water into a 500-mL volumetric flask.

7.4. Add 1.25 mL of concentrated HNO_3 to the water in the flask to reach a pH of approximately 1.

7.5. Spike an aliquot of gross gamma standard into the flask to reach a gross gamma concentration in the desired spike range.

7.6. Fill the volumetric flask to volume with distilled water and mix by inverting.

7.7. Transfer the solution to a 500-mL, high-density polyethylene bottle and label the bottle with a QC sample number.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Calculate the gross gamma concentration of a ^{137}Cs standard as in the following example.

8.1.1. If the lower energy threshold of the analytical method used to measure the QC samples is 100 keV, only 0.851 of the gamma radiation emitted by ^{137}Cs is at an energy level (662 keV) exceeding the lower threshold energy and may be used to determine gross gamma concentration.

8.1.2. A standard with a ^{137}Cs concentration of 6000 pCi/mL has a gross gamma concentration with energy levels exceeding 100 keV of 5106 pCi/mL.

$$\left(\frac{6000\ \text{pCi}}{1\ \text{mL}}\right)(0.851) = 5106\ \text{pCi/mL}\ .$$

8.2. Calculate the gross gamma concentration of the QC sample as in the following example.

8.2.1. If 100 µL of a 5106-pCi/mL gross gamma standard is used to spike 500 mL of acidified water, the concentration of gross gamma in the acidified water will be 1021 pCi/L.

$$\frac{(5106\ \text{pCi/mL})\ (100\ \mu\text{L})\ (\frac{1\ \text{mL}}{1000\ \mu\text{L}})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 1021\ \text{pCi/L}\ .$$

8.2.2. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

8.2.3. Record the concentration of gross gamma in the QC sample as nCi/L or pCi/L.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4233-B, Cesium-137 Burn-Up Standard" (Washington, DC, November 1979).

10.2. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.3. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM AND AMERICIUM ON SOIL — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR160
Matrix: Soil	**Spike Range:** 0.1–1 pCi/g
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** ^{238}Pu 100% ± 3.4% RSD ^{239}Pu 100% ± 3.1% RSD ^{241}Am 100% ± 4.5% RSD
Effective Date: 04/12/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.5 and 10.6 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the pipette and of the balance. Relative standard deviations (RSDs) of 3.4% for ^{238}Pu, 3.1% for ^{239}Pu, and 4.5% for ^{241}Am at the 1-σ level have been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2 Analytical results from QC samples prepared between 1991 and 1993 using this procedure and analyzed by radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Materials 10.3. and 10.4.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM ON SOIL

	Radionuclide	Mean ± std dev (%)	Number of Samples
1991	^{238}Pu	99 ± 7	17
	^{239}Pu	103 ± 10	22
	^{241}Am	95 ± 8	11
1992	^{238}Pu	103 ± 19	75
	^{239}Pu	98 ± 12	59
	^{241}Am	108 ± 19	41
1993	^{238}Pu	100 ± 8	97
	^{239}Pu	105 ± 12	91
	^{241}Am	98 ± 8	49

3. Collection and Storage of Samples

3.1. Spiked QC samples are stored at room temperature pending analysis.

4. Apparatus

4.1. Bottles: 500-mL, high-density polyethylene.

4.2. Balance: 200-g capacity, 0.1-mg accuracy.

4.3. Auto-pipette: 100-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Spatula.

4.6. Heat lamp.

4.7. Labels printed with QC sample numbers.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless-steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Sand. A clean and dry 10-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. QC samples are spiked with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. The plutonium standards are heated at 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state.

6.2. The radionuclide standards should have concentrations of approximately 180 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as National Bureau of Standards (NBS) Standard Reference Material (SRM) 4323. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. All solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure it is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 10 g sample aliquot in a 500-mL high-density polyethylene bottle.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically analyze a 10-g aliquot of the unspiked sand as a blank.

7.3. Accurately weigh 10 g of clean, dry sand into a 500-mL high-density polyethylene bottle. Record the weight of sand on the polyethylene bottle with a felt-tipped pen for reference by the analyst.

7.4. Spike aliquots of the Pu and Am standard solutions onto the sand to reach the desired spike range.

7.5. Air-dry the samples or dry under a heat lamp until excess liquid is gone.

7.6. Cap the sample bottles and label with a QC sample number. The entire contents of the bottle must be analyzed.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 20 μL of a 175-pCi/mL ^{238}Pu standard is used to spike 10.0000 g of sand, the ^{238}Pu concentration in the sand is 0.35 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(175\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{\text{mL}}{1000\ \mu\text{L}}\right)(20\ \mu\text{L})}{10.0000\ \text{g}} = 0.35\ \text{pCi/g}$$

8.3. Spike concentrations for ^{239}Pu and ^{241}Am are calculated like spike concentrations for ^{238}Pu using the equation in Step 8.2.1.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste Pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.6. National Bureau of Standards, "Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.7. National Bureau of Standards, "Standard Reference Material 4331, Plutonium-239 Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, March 1975).

10.8. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

RADIONUCLIDES ON VEGETATION ASH — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, Americium-241, and Strontium-90	**Method No:** QCR170
Matrix: Vegetation ash	**Spike Range:** 1–10 pCi/g
Procedure: Radiochemistry and alpha spectrometry or gas-flow proportional counting	**Accuracy and Precision:** ^{238}Pu 100% ± 3.5% RSD ^{239}Pu 100% ± 3.2% RSD ^{241}Am 100% ± 4.5% RSD ^{90}Sr 100% ± 3.2% RSD
Effective Date: 06/15/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.3 and 10.4 for proper waste disposal practices.

1. Principle of Method

1.1. Blank vegetation ash is spiked with ^{238}Pu, ^{239}Pu, ^{241}Am, and ^{90}Sr standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. Relative standard deviations (RSDs) of 3.5% for ^{238}Pu, 3.2% for ^{239}Pu, 4.5% for ^{241}Am, and 3.2% for ^{90}Sr at the 1-σ level have been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} \quad ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 \quad ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2 Analytical results from QC samples prepared between 1991 and 1993 using this procedure and analyzed by gas-flow proportional counting or radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

		Spike range, pCi/g	Mean ± std dev %	Number of Samples
^{238}Pu				
	1991	1.0 - 5.0	113.0	1
		5.0 - 10.0	109 ± 2	3
	1992	1.0 - 5.0	108 ± 7	3
	1993	1.0 - 5.0	99 ± 8	9
		5.0 - 10.0	98 ± 0.6	2
^{239}Pu				
	1991	1.0 - 5.0	105 ± 1	4
		5.0 - 10.0	106.9	1
	1992	1.0 - 5.0	105 ± 5	3
	1993	1.0 - 5.0	99 ± 4	9
		5.0 - 10.0	103 ± 6	3
^{241}Am				
	1992	1.0 - 5.0	87.9	1
^{90}Sr				
	1991	1.0 - 5.0	135 ± 17	4
		5.0 - 10.0	114 ± 11	4
	1992	1.0 - 5.0	108 ± 20	2
	1993	1.0 - 5.0	109 ± 9	6
		5.0 - 10.0	94 ± 9	6

3. Collection and Storage of Samples

3.1. Spiked QC samples are covered with plastic wrap and stored at room temperature pending analysis.

4. Apparatus

4.1. Beakers: 600-mL, glass.

4.2. Balance: 300-g capacity, 0.1-mg accuracy.

4.3. Auto-pipette: 100-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Plastic wrap.

4.6. Labels printed with QC sample numbers.

4.7. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.8. Discs: stainless-steel, 2.22-cm-diam.

4.9 Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.10. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.11. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Vegetation ash. A 1-g aliquot is required for each sample.

5.2. A suitable vegetation ash does not contain the analyte of interest and presents few interferences to the analytical method. Commercially available dry pet or farm stock foods may provide a suitable vegetation ash. Previously analyzed vegetation ash samples that did not contain Pu, Am, or Sr may also be used as a QC matrix.

6. Calibration and Standards

6.1. QC samples are spiked with either ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3, an ^{241}Am standard prepared in 4 N HNO_3, or a ^{90}Sr standard prepared in 2 M HCl. The plutonium standards are heated at 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state.

6.2. The radionuclide standards should have concentrations of approximately 180 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as National Bureau of Standards (NBS) Standard Reference Material (SRM) 4323. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook

6.8. The Pu and Am solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure it is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.10. The ^{90}Sr standard should be calibrated against a NIST or an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.11. Decay the ^{90}Sr standards each year

6.11.1. The half-life of ^{90}Sr is 28.5 years.

6.11.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically analyze a 1-g aliquot of the unspiked vegetation ash as a blank.

7.2. Accurately weigh 1 g of vegetation ash into a 600-mL beaker. Record the weight of the ash on the beaker with a felt-tipped pen for reference by the analyst.

7.3. Spike aliquots of the Pu, Am, or Sr standard solutions onto the vegetation ash to reach the desired spike range.

7.4. Cover the beaker with plastic wrap and label it with a QC sample number. The entire contents of the beaker must be analyzed.

7.5. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, ^{241}Am, and ^{90}Sr on the vegetation ash as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 15 μL of a 175-pCi/mL ^{238}Pu standard is used to spike 1.0000 g of vegetation ash, the ^{238}Pu concentration in the ash is 2.6 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(175\ \frac{pCi}{mL}\right)\left(\frac{1\ mL}{1000\ \mu L}\right)(15\ \mu L)}{1.0000\ g} = 2.6\ pCi/g$$

8.3. Spike concentrations for ^{239}Pu, ^{241}Am, and ^{90}Sr are calculated like spike concentrations for ^{238}Pu using the equation in Step 8.2.1.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid water that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, and G. H. Brooks, W. D. Moss, "Quality Assurance Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992, " Los Alamos National Laboratory report LA-12790-MS (1993).

10.3. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.4. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.6. National Bureau of Standards, "Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.7. National Bureau of Standards, "Standard Reference Material 4331, Plutonium-239 Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, March 1975).

10.8. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

Revisions or additions to the procedure are marked (▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM AND AMERICIUM IN WATER — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR180
Matrix: Water	**Spike Range:** 0.1 to 5 pCi/L
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** ^{238}Pu 100% ± 5.1% RSD ^{239}Pu 100% ± 1.7% RSD ^{241}Am 100% ± 1.9% RSD
Effective Date: 08/02/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.7 and 10.8 for proper waste disposal practices.

1. Principle of Method

1.1. Acidified blank water is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the volumetric flask and of the pipette. Relative standard deviations (RSDs) of 5.1% for ^{238}Pu, 1.7% for ^{239}Pu, and 1.9% for ^{241}Am at the 1-σ level have been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2 Analytical results from QC samples prepared between 1991 and 1993 using this procedure and analyzed by radiochemistry and alpha spectrometry are summarized in Table I below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM IN WATER

	Radionuclide	Mean ± std dev (%)	Number of Samples
1991	^{238}Pu	102 ± 10	12
	^{239}Pu	105 ± 14	13
	^{241}Am	90 ± 2	5
1992	^{238}Pu	104 ± 10	21
	^{239}Pu	108 ± 22	20
	^{241}Am	98 ± 18	12
1993	^{238}Pu	104 ± 13	22
	^{239}Pu	106 ± 14	30
	^{241}Am	93 ± 10	13

3. Collection and Storage of Samples

3.1. QC samples are prepared in an acid medium in a volumetric flask and are stored in the flask at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 500-mL, glass, class A.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Pipette: 2-mL, class A volumetric.

4.5. Labels printed with QC sample numbers.

4.6. Heat lamp.

4.7. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.8. Discs: stainless-steel, 2.22-cm-diam.

4.9. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.10. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.11. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. The plutonium standards are heated at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state.

6.2. The concentration of the ^{238}Pu, ^{239}Pu, and ^{241}Am standards should be between approximately 2 pCi/mL and 6 pCi/mL.

6.3. When they are available, certified primary standards should be diluted to make standards at the desired concentration.

6.4. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.5. The ^{238}Pu standard should be calibrated against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as National Bureau of Standards (NBS) Standard Reference Material (SRM) 4323. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. The ^{239}Pu standard should be calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as NBS SRM 4331. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. The ^{241}Am standard should be calibrated against a NIST-certified ^{241}Am alpha-particle solution standard, such as NBS SRM 4322. The standard solution should be recalibrated yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. All solutions are counted on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs and evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures a tightly sealed package when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

6.10. Alternatively, an Environmental Protection Agency (EPA) Plutonium in Water crosscheck sample may be used as a QC sample. After dilution and distribution of a crosscheck study, Environmental Chemistry (CST-9) transfers the remainder of the stock solution to a glass container for storage to prevent the loss of the radionuclides to the walls of the EPA polyethylene container.

6.10.1. The EPA records the concentration of the standard after dilution according to EPA instructions.

6.10.2. The concentration of the original stock solution must be back-calculated before it is used, taking the EPA dilution instructions into consideration.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 500-mL sample aliquot in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include an unspiked water sample acidified to 3 N with HCl as a blank.

7.3. Place approximately 300 mL of distilled water into a 500-mL volumetric flask.

7.4. Add 125 mL of 12 M HCl to produce a final acid concentration of 3 M.

7.5. Spike aliquots of the Pu and Am standard solutions into the water to reach the desired spike range.

7.6. Dilute the QC sample to volume using distilled water. Mix by inversion. Label the flask with a QC sample number and store at room temperature pending analysis.

7.7. EPA crosscheck standard.

7.7.1. The EPA standard contains only plutonium.

7.7.2. Back-calculate the concentration of the original stock before an aliquot is taken. See Step 8.3.

7.7.3. EPA recommends mixing the standard for 10 to 15 min before an aliquot is taken.

7.8. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am in the water as pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 300 μL of a 2-pCi/mL ^{238}Pu standard is used to spike 450 mL of acidified water and the solution is diluted to 500 mL, the ^{238}Pu concentration in the acidified water is 1.2 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(2\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (300\ \mu\text{L})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 1.2\ \text{pCi/L} \quad .$$

8.2.2. Spike concentrations for ^{239}Pu and ^{241}Am are calculated like spike concentrations for ^{238}Pu using the equation in Step 8.2.1.

8.3. If an EPA crosscheck Plutonium in Water sample will be used to make a QC standard for plutonium in water, the undiluted concentration of the crosscheck sample must first be calculated.

8.3.1. If the concentration of the EPA sample is 10.6 ± 1.1 pCi/L after dilution of a 500-mL aliquot to 4 L, the concentration of the undiluted sample is calculated as follows:

$$(10.6\ \text{pCi/L})\ (4\ \text{L}/500\ \text{mL})\ (1000\ \text{mL/L}) = 84.8\ \text{pCi/L} \quad .$$

The concentration of 84.8 pCi/L is then used to determine the aliquot used to spike the acidified water sample.

8.3.2. If 4 mL of the 84.8-pCi/L EPA sample is spiked into 400 mL of acidified water and is diluted to 500 mL with distilled water, the plutonium concentration is 0.68 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(84.8\ \text{pCi/L})\ (1\ \text{L}/1000\ \text{mL})\ (4\ \text{mL})}{(500\ \text{mL})\ (1\ \text{L}/1000\ \text{mL})} = 0.68\ \text{pCi/L}\ .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.4. National Bureau of Standards, "Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, November 1986).

10.5. National Bureau of Standards, "Standard Reference Material 4331, Plutonium-239 Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, Maryland, March 1975).

10.6. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.7. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.8. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM-238 IN URINE — QC SAMPLE PREPARATION

Analyte: Plutonium-238	**Method No.:** QCR190
Matrix: Urine	**Spike Range:** 0.0-0.40 pCi/sample
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 3.7% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.11 to 10.13 for proper waste disposal.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with the use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 3.7% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$SD_T = \sqrt{\frac{\left[R_{M1}^2 (M_3 + M_2)^2 + M_3^2 (R_{M2}^2 + R_{M3}^2)\right]}{(M_3 + M_2)^2}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
M_3 = volume of cylinder,
M_2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2. Analysis by radiochemistry and alpha spectrometry of QC samples prepared between 1984 and 1989 using this procedure gave a mean recovery of 99% ± 14% RSD. The data are published in Source Materials 10.1 through 10.6 and are summarized in Table I below.

TABLE I. PLUTONIUM-238 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY

Year	Spike level pCi/sample	Mean ± RSD (%)	Number of samples
1984	0.06	82 ± 20	13
	0.12	93 ± 12	15
	0.20	89 ± 11	14
	0.40	89 ± 9	16

TABLE I. PLUTONIUM-238 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY (cont)

Year	Spike level pCi/sample	Mean ± RSD (%)	Number of samples
1985	0.06	98 ± 20	9
	0.12	97 ± 17	18
	0.20	100 ± 14	11
	0.40	103 ± 7	11
1986	0.06	97 ± 21	13
	0.12	104 ± 11	14
	0.20	103 ± 11	11
	0.40	110 ± 8	11
1987	0.06	102 ± 16	12
	0.12	95 ± 11	11
	0.19	105 ± 5	12
	0.39	96 ± 10	12
1988	0.06	102 ± 22	13
	0.12	97 ± 7	13
	0.19	102 ± 10	14
	0.39	100 ± 8	13
1989	0.06	102 ± 24	18
	0.12	99 ± 10	16
	0.19	114 ± 18	15
	0.39	100 ± 15	12

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work and is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 500-mL.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 16-oz jars with screw caps.

4.6. Labels printed with QC sample numbers.

4.7. Heat lamp.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{238}Pu standard prepared in 2 N HNO_3 and heated at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.2. The ^{238}Pu standard should be at a concentration of approximately 0.8 pCi/mL.

6.3. The ^{238}Pu standard was calibrated against a NIST-certified ^{238}Pu alpha-particle solution standard, such as SRM 4323. Recalibrate the standard solution yearly by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.4. Direct plating procedure.

6.4.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, then evaporate to dryness under a heat lamp.

6.4.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper assures a tightly sealed package when assembled.

6.4.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.4.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.4.5. Place a piece of Mylar film over all the layers.

6.4.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.4.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.4.8. The count room data are corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Remove gloves, discard them in the biohazard waste container, and wash hands with soap and water.

7.2. Prepare a pool from blank urine sufficient in volume to allow 400 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples.

7.4. Record QC standard information, sample spike amount, concentration, and uncertainty in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 400 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentrations of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Record spike concentrations as pCi/sample of urine.

8.2. Calculate the spike concentration for a 150-μL aliquot of ^{238}Pu standard using the following equation.

$$\text{pCi/sample per spike amount} = (0.8\ \text{pCi/mL}) \times 0.150\ \text{mL} = 0.12\ \text{pCi/sample}$$

8.3. Spike concentrations calculated in Step 8.2 are tabulated below.

Spike amount (μL)	Concentration (pCi/sample)	Uncertainty (± 3.7%)
75	0.06	0.002
150	0.12	0.004
250	0.20	0.007
500	0.40	0.015

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. Dispose of bottles used to collect blank urine for a QC sample matrix as uncontaminated laboratory trash after they have been rinsed with dilute bleach solution.

9.2.2.2. Accumulate solid waste (such as paper wipes, plastic pipettes, and rubber gloves contaminated with biohazardous material, primarily urine) in a plastic bag labeled for the collection of biohazardous waste and keep it segregated from waste with no biohazard contamination.

9.2.2.3. Transfer full bags of biohazardous waste to a cardboard box labeled with a biohazard label and lined with a plastic bag bearing a biohazard label.

9.2.2.4. When the cardboard box is full, seal the liner bag and the box.

9.2.2.5. Line a new biohazard waste box with a plastic bag for further use.

9.3. Waste pickup.

9.3.1. Radiochemically contaminated waste.

9.3.1.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.1.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.2. Biohazardous waste.

9.3.2.1. Request CST-7 to pick up a full box of biohazardous waste using the current Chemical Waste Disposal Request (CWDR)

form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2.2. CST-7 arranges for pickup and disposal of the waste by the company currently under contract with the Laboratory for that purpose.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

10.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

10.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

10.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

10.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

10.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.7. *EML Procedures Manual*, 25th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.8. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4323, Plutonium-238 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, November 1986).

10.9. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Institute of Standards and Technology, Washington, DC, April 1982).

10.10. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.11. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.12. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.13. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

PLUTONIUM-239 IN URINE — QC SAMPLE PREPARATION

Analyte: Plutonium-239	**Method No.:** QCR200
Matrix: Urine	**Spike Range:** 0.0-0.46 pCi/sample
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.11 to 10.13 for proper waste disposal.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$SD_T = \sqrt{\frac{\left[R^2_{M1} (M_3 + M_2)^2 + M_3^2 (R^2_{M2} + R^2_{M3})\right]}{(M_3 + M_2)^2}} \times 100 ,$$

where SD_T = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
M_3 = volume of cylinder,
M_2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2. Analysis by radiochemistry and alpha spectrometry of QC samples prepared between 1984 and 1989 using this procedure gave a mean recovery of 101% ± 12% RSD. The data are published in Source Materials 10.1 to 10.6 and are summarized in Table I below.

TABLE I. PLUTONIUM-239 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY

Year	Spike level pCi/sample	Mean ± RSD (%)	Number of samples
1984	0.06	96 ± 24	13
	0.15	99 ± 12	14
	0.23	99 ± 7	13
	0.46	96 ± 4	15
	1.47	89 ± 15	15

TABLE I. PLUTONIUM-239 SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION AFTER CORRECTION FOR PLUTONIUM-242 RECOVERY (cont)

Year	Spike level pCi/sample	Mean ± RSD (%)	Number of samples
1985	0.06	102 ± 20	13
	0.15	108 ± 11	11
	0.23	98 ± 13	8
	0.45	110 ± 10	6
	1.50	96 ± 7	10
1986	0.06	108 ± 15	15
	0.15	107 ± 14	14
	0.23	100 ± 11	14
	0.46	100 ± 11	14
1987	0.06	105 ± 13	15
	0.15	105 ± 8	14
	0.22	102 ± 10	13
	0.44	103 ± 11	11
1988	0.06	99 ± 22	16
	0.15	96 ± 6	13
	0.22	99 ± 12	15
	0.44	103 ± 8	12
1989	0.06	98 ± 26	15
	0.15	99 ± 12	13
	0.22	101 ± 11	17
	0.44	100 ± 8	17

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work and is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 500-mL.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 16-oz jars with screw caps.

4.6. Labels printed with QC sample numbers.

4.7. Heat lamp.

4.8. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.9. Discs: stainless steel, 2.22-cm-diam.

4.10. Alpha phosphor on Mylar: The phosphor is the standard silver-activated zinc sulfide. William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.11. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon, Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.12. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick, manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with a ^{239}Pu standard prepared in 2 N HNO_3 and heated at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic 4+ state. The solution is counted on a zinc sulfide scintillation system calibrated with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.2. The ^{239}Pu standard should be at a concentration of approximately 1.5 pCi/mL.

6.3. The ^{239}Pu standard was calibrated against a NIST-certified ^{239}Pu alpha-particle solution standard, such as SRM 4331. Recalibrate the standard solution yearly

by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.4. Direct plating procedure.

6.4.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on each of six 2.22-cm stainless-steel discs, then evaporate to dryness under a heat lamp.

6.4.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper assures a tightly sealed package when assembled.

6.4.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disk is centered.

6.4.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.4.5. Place a piece of Mylar film over all the layers.

6.4.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.4.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) per sample count.

6.4.8. The count room data are corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Remove gloves, discard them in the biohazard waste container, and wash hands with soap and water.

7.2. Prepare a pool from blank urine sufficient in volume to allow 400 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples.

7.4. Record QC standard information, sample spike amount, concentration, and uncertainty in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 400 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentrations of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Record spike concentrations as pCi/sample of urine.

8.2. Calculate the spike concentration for a 300-μL aliquot of ^{239}Pu standard using the following equation:

$$x = (1.52 \text{ pCi/mL}) \times 0.300 \text{ mL} = 0.46 \text{ pCi/sample} ,$$

where x = pCi/sample per spike amount.

8.3. Spike concentrations calculated in Step 8.2 are tabulated below.

Spike amount (μL)	Concentration (pCi/sample)	Uncertainty (± 3.3%)
40	0.06	0.002
100	0.15	0.005
150	0.23	0.008
300	0.46	0.015

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. Dispose of bottles used to collect blank urine for a QC sample matrix as uncontaminated laboratory trash after they have been rinsed with dilute bleach solution.

9.2.2.2. Accumulate solid waste (such as paper wipes, plastic pipettes, and rubber gloves contaminated with biohazardous material, primarily urine) in a plastic bag labeled for the collection of biohazardous waste and keep it segregated from waste with no biohazard contamination.

9.2.2.3. Transfer full bags of biohazardous waste to a cardboard box labeled with a biohazard label and lined with a plastic bag bearing a biohazard label.

9.2.2.4. When the cardboard box is full, seal the liner bag and the box.

9.2.2.5. Line a new biohazard waste box with a plastic bag for further use.

9.3. Waste pickup.

9.3.1. Radiochemically contaminated waste.

9.3.1.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.1.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.2. Biohazardous waste.

9.3.2.1. Request CST-7 to pick up of a full box of biohazardous waste using the current Chemical Waste Disposal Request

(CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2.2. CST-7 arranges for pickup and disposal of the waste by the company currently under contract with the Laboratory for that purpose.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

10.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

10.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

10.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

10.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

10.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.7. *EML Procedures Manual*, 25th ed., H. L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.8. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4331, Plutonium-239 Alpha-Particle Solution Standard" (National Institute of Standards and Technology, Washington, DC, March 1975).

10.9. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Institute of Standards and Technology, Washington, DC, April 1982).

10.10. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.11. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.12. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.13. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

RADIONUCLIDES ON FILTER MEDIA — QC SAMPLE PREPARATION

Analyte: Plutonium-238, Plutonium-239, and Americium-241	**Method No.:** QCR210
Matrix: Filters	**Spike Range:** 0.45–2.25 pCi/filter
Procedure: Radiochemistry and alpha spectrometry	**Accuracy and Precision:** ^{238}Pu 100% ± 4.3% RSD ^{239}Pu 100% ± 1.9% RSD ^{241}Am 100% ± 1.9% RSD
Effective Date: 01/21/85	**Authors:** Margaret A. Gautier Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.8 and 10.9 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is placed on a Microsorban filter and is spiked with ^{238}Pu, ^{239}Pu, and ^{241}Am standards. The standards are spiked onto sand because the filters are hydrophobic.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six sample plate preparations of the standard and on the error associated with use of the pipette. A relative standard deviation (RSD) of 4.3% for ^{238}Pu, 1.9% for ^{239}Pu, and 1.9% for ^{241}Am at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = calibration error, and
M2 = spiking error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1991 and 1993 using this procedure and analyzed by radiochemistry and alpha spectrometry are tabulated below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY FOR PLUTONIUM AND AMERICIUM ON FILTERS

	Radionuclide	Mean ± std dev (%)	Number of Samples
1991	^{238}Pu	100 ± 7	9
	^{239}Pu	91 ± 8	9
	^{241}Am	94 ± 4	9
1992	^{238}Pu	100 ± 6	11
	^{239}Pu	100 ± 8	11
	^{241}Am	86 ± 7	11
1993	^{238}Pu	104 ± 7	23
	^{239}Pu	106 ± 7	23
	^{241}Am	88 ± 7	16

3. Collection and Storage of Samples

3.1. Microsorban filters are obtained from the sample submitter.

3.2. QC samples are prepared in a platinum crucible with a platinum cover and are kept at room temperature pending analysis.

4. Apparatus

4.1. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.2. Pipette tips: disposable.

4.3. Balance: 100-g minimum capacity, 0.1-mg accuracy.

4.4. Spatula.

4.5. Platinum crucibles: approximately 50-mL capacity with platinum covers. Each crucible should have a unique identifying number stamped or etched into it.

4.6. Heat lamp.

4.7. Microsorban filters: 8-cm-diam polyethylene filter obtained from the sample submitter.

4.8. Labels printed with QC sample numbers.

4.9. Filter paper: 2.9-cm, Whatman No. 41 or equivalent.

4.10. Discs: stainless-steel, 2.22-cm-diam.

4.11. Alpha phosphor on Mylar: the phosphor is the standard silver-activated zinc sulfide, William B. Johnson & Associates, Inc., Research Park, Montville, NJ 07045.

4.12. Rings and discs: plastic rings and discs, nominal 1-in.-diam, molded of nylon. Control Molding Corp., 84 Granite Ave., Staten Island, NY 10303.

4.13. Mylar film: 1.5-in.-wide rolls, 0.0005 in. thick. Manufactured by E. I. duPont de Nemours, retailed by Brownell, Inc., 85 Tenth Ave., New York, NY 10001.

5. Reagents

5.1. Sand. A clean, dry 0.1-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. Spike QC samples with ^{238}Pu and ^{239}Pu standards prepared in 2 N HNO_3 and with an ^{241}Am standard prepared in 4 N HNO_3. Heat the plutonium standards at a nominal temperature of 80°C for 2 h to convert Pu in the polymeric form to the ionic +4 state. Count all solutions on a zinc sulfide scintillation system calibrated with National Bureau of Standards (NBS) Standard Reference Material (SRM) 4904L-F, an ^{241}Am alpha-particle standard.

6.2. The ^{239}Pu standard should be at a concentration of approximately 2 pCi/mL. The ^{238}Pu and ^{241}Am standards should be at a concentration of approximately 17 pCi/mL.

6.3. When they are available, dilute certified primary standards to make standards at the desired concentration.

6.4. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.5. Calibrate the ^{238}Pu standard against a National Institute of Standards and Technology (NIST)-certified ^{238}Pu alpha-particle solution standard, such as NBS SRM 4323. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.6. Calibrate the ^{239}Pu standard against a NIST-certified ^{239}Pu alpha-particle solution standard such as NBS SRM 4331. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.7. Calibrate the ^{241}Am standard against a NIST-certified ^{241}Am alpha-particle solution standard such as NBS SRM 4322. Calibrate the standard solution annually by direct plating and alpha scintillation counting. Record all data in the QC Laboratory notebook.

6.8. Count all solutions on a zinc sulfide scintillation system calibrated with NBS SRM 4904L-F, an ^{241}Am alpha-particle standard, using Method No. CR340.

6.9. Direct plating procedure.

6.9.1. Pipette a 200- to 300-μL aliquot of the standard to be calibrated on to each of six 2.22-cm stainless-steel discs. Evaporate to dryness under a heat lamp.

6.9.2. Place a 2.9-cm filter paper on a molded nylon disc. The filter paper ensures the package is tightly sealed when assembled.

6.9.3. Place the stainless-steel disc containing the sample on the filter paper, making sure the disc is centered.

6.9.4. Place a 0.875-in. phosphor paper over the stainless-steel disc (dull side against the disc).

6.9.5. Place a piece of Mylar film over all the layers.

6.9.6. Press a nylon ring down over the layers and around the nylon disc to form a tightly sealed package. Cut off the excess Mylar with scissors. Label the back of the assembly with an identification number.

6.9.7. Submit the samples to the count room for alpha scintillation counting and request a 60,000-s (overnight) count for each sample.

6.9.8. The count room data is corrected for background and reported in disintegrations per minute (dis/min). Divide the dis/min results by 2.22 to convert to pCi. Calculate the mean and standard deviation of the six plates and assign the value to the standard.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically submit an unspiked filter as a blank.

7.2. Cut a Microsorban filter in half and fold it so that it fits into a 50-mL platinum crucible.

7.3. Place the crucible with the filter on the balance and tare the balance.

7.4. Weigh 0.1 g of clean, dry sand onto the filter. Because the filter is hydrophobic, the sand is used to absorb the Pu and Am standard solutions.

7.5. Spike aliquots of the Pu and Am standard solutions onto the sand to reach the desired spike range.

7.6. Dry the spiked sand and filter under a heat lamp.

7.7. A paper label should not be affixed to the platinum crucible because it will be destroyed during the ashing procedure.

7.8. Assign a QC sample number to the QC sample and note the unique identifying number that is etched or stamped onto the platinum crucible body. Make a list of the QC sample numbers and the corresponding crucible number.

7.9. When the sample is dry, cover the crucible with a platinum cover and keep it at room temperature pending analysis.

7.10. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{238}Pu, ^{239}Pu, and ^{241}Am on the filter as pCi/filter.

8.2. Calculate the spike concentrations as in the following example.

8.2.1. The weight of the sand placed on top of the filter does not enter into the calculation.

8.2.2. If 80 μL of a 16.42-pCi/mL ^{238}Pu standard is spiked onto sand on the Microsorban filter, the ^{238}Pu concentration in the filter will be 1.3 pCi/filter. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(16.42\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (80\ \mu\text{L})}{\text{filter}} = 1.3\ \text{pCi/filter} \quad .$$

8.3. Spike concentrations for ^{239}Pu and ^{241}Am are calculated in the same way as spike concentrations for ^{238}Pu, using the equation in Step 8.2.2.

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. *EML Procedures Manual*, 25th ed., H.L. Volchok and G. de Planque, Eds. (Environmental Measurements Laboratory, New York, August 1982).

10.4. National Bureau of Standards, "Standard Reference Material 4323, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

10.5. National Bureau of Standards, "Standard Reference Material 4322, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, November 1986).

10.6. National Bureau of Standards, "Standard Reference Material 4331, Alpha-Particle-Solution Standard" (National Bureau of Standards, Gaithersburg, MD, March 1975).

10.7. National Bureau of Standards, "Standard Reference Material 4904L-F, Alpha-Particle Standard" (National Bureau of Standards, Washington, DC, April 1982).

10.8. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.9. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

RADIUM-226 IN WATER — QC SAMPLE PREPARATION

Analyte: Radium-226	**Method No.:** QCR220
Matrix: Water	**Spike Range:** 0.5–5.0 pCi/L
Procedure: Proportional counting or radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 2.1% RSD
Effective Date: 02/05/90	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of ^{226}Ra in water is prepared by spiking 0.12 M HCl with a ^{226}Ra standard.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 2.1% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analytical results from QC samples prepared between 1990 and 1993 using this procedure and analyzed by proportional counting or by radiochemistry and alpha spectrometry are tabulated below. The data are published in Source Materials 10.1 through 10.3.

TABLE I. SPIKE RECOVERY FOR RADIUM-226 IN WATER

	Mean ± std dev	Number of Samples
1990	65 ± 25	4
1991	82 ± 19	8
1992	93 ± 17	4
1993	98 ± 19	4

3. Collection and Storage of Samples

3.1. QC samples are stored in volumetric flasks at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 1-L.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Labels printed with QC sample numbers.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. QC samples are spiked with a ^{226}Ra standard in 0.1 M HNO_3 at a concentration of approximately 10 pCi/mL.

6.2. A certified ^{226}Ra standard, such as National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4958 (gamma-ray standard), is diluted to produce a standard with a ^{226}Ra concentration of approximately 10 pCi/mL.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 1-L sample aliquot in a volumetric flask.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include 1 L of 0.12 M HCl as a blank.

7.3. Add approximately 900 mL of distilled water to a 1-L volumetric flask.

7.4. Add 10 mL of 12 M HCl to the water in the flask to produce 0.12 M acid.

7.5. Add an aliquot of ^{226}Ra standard to the water in the flask to reach the desired spike range.

7.6. Dilute the QC sample to volume with distilled water. Mix by inversion. Label the flask with a QC sample number and store at room temperature pending analysis.

7.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{226}Ra in the QC sample as pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 220 μL of a 10-pCi/mL ^{226}Ra standard is used to prepare a 1-L QC sample, the ^{226}Ra concentration in the sample will be 2.2 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(10\ \text{pCi/mL})\ (1\ \text{mL}/1000\ \mu\text{L})\ (220\ \mu\text{L})}{1\ \text{L}} = 2.2\ \text{pCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid waste that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste Pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991, " Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992, " Los Alamos National Laboratory report LA-12790-MS (1994).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. National Institute of Standards and Technology, "Certificate of Analysis for Radium-226" (National Institute of Standards and Technology, Washington, DC, March 1968).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

STRONTIUM-90 ON SOIL — QC SAMPLE PREPARATION

Analyte: Strontium-90	**Method No.:** QCR230
Matrix: Sand	**Spike Range:** 5–45 pCi/g
Procedure: Proportional counting or radiochemistry and alpha spectrometry	**Accuracy and Precision:** 100% ± 3.0% RSD
Effective Date: 04/07/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is spiked with a ^{90}Sr standard. The sand is used in place of soil as the quality control (QC) matrix for ^{90}Sr analysis.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the balance. A relative standard deviation (RSD) of 3.0% at the 1-σ level has been calculated for the calibration, spiking, and weighing process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = weighing error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$SD_T = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of balance, and
100 = factor to convert to percentage.

2.2. Analytical results from samples prepared between 1991 and 1993 using this procedure and analyzed by proportional counting or radiochemistry and alpha spectrometry are tabulated below. The data are published in Source Materials 10.1 and 10.2.

TABLE I. SPIKE RECOVERY FOR STRONTIUM-90 IN SOIL

	Mean ± std dev (%)	Number of Samples
1991	89 ± 15	19
1992	99 ± 9	58
1993	92 ± 11	52

3. Collection and Storage of Samples

3.1. Pending analysis, QC samples are stored at room temperature in Teflon beakers covered with aluminum foil.

4. Apparatus

4.1. Beakers: 250-mL, Teflon.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Balance: 200-g capacity, 0.1-mg accuracy.

4.5. Spatula.

4.6. Aluminum foil.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. Sand. A clean and dry 2-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

NOTE: Surface soils have been contaminated with radionuclides as a result of the use and testing of nuclear weapons. A suitable blank soil for this procedure would have been collected before World War II or would be collected from a deep well or other excavation where radioactive contamination is not likely to have occurred. Before use, a representative aliquot of soil is analyzed to determine if it will provide a suitably blank matrix.

6. Calibration and Standards

6.1. When they are available, certified primary standards should be diluted to make a standard at the desired concentration.

6.2. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.3. QC samples are spiked with a ^{90}Sr standard prepared in 2 M HCl at a concentration of approximately 870 pCi/mL.

6.4 The ^{90}Sr standard should be calibrated against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.5. Decay the ^{90}Sr standards each year.

6.5.1. The half-life of ^{90}Sr is 28.5 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 2-g sample in a 250-mL Teflon beaker.

7.2. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include a 2-g aliquot of the unspiked deep-well sand as a blank.

7.3. Accurately weigh a 2-g aliquot of clean, dry sand into a 250-mL Teflon beaker. Record the weight of the sand on the beaker with a felt-tipped pen for reference by the analyst.

7.4. Spike an aliquot of ^{90}Sr standard onto the sand to reach the desired spike range.

7.5. Because a paper label does not adhere well to a Teflon beaker, write the QC number assigned to the sample on the beaker with a pen and destroy the paper label associated with the sample number used. Cover the top of the beaker with aluminum foil and store it at room temperature pending analysis.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{90}Sr on the sand as pCi/g.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 15 μL of a 871-pCi/mL ^{90}Sr standard is used to spike 2.0000 g of sand, the ^{90}Sr concentration in the sand will be 6.5 pCi/g. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(871\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(15\ \mu\text{L})}{2.0000\ \text{g}} = 6.5\ \text{pCi/g}\ .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of liquid water that is radioactively contaminated in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the period of time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. US Environmental Protection Agency, "Calibration Certificate for Strontium-90" (Environmental Monitoring Systems Laboratory, Quality Assurance Division, Las Vegas, Nevada, June 1987).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, in Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised

STRONTIUM-90 IN WATER — QC SAMPLE PREPARATION

Analyte: Strontium-90	**Method No.:** QCR240
Matrix: Water	**Spike Range:** 8-400 pCi/L
Procedure: Proportional counting	**Accuracy and Precision:** 100% ± 3.2 % RSD
Effective Date: 11/28/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.4 and 10.5 for proper waste disposal.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of ^{90}Sr in water is prepared by spiking 0.08 M HCl with a ^{90}Sr standard.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and the volumetric flask. A relative standard deviation (RSD) of 3.2% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{R^2_{M1} + R^2_{M2} + R^2_{M3}} \times 100 ,$$

where S_{D_T} = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by proportional counting of QC samples (N = 16) prepared from 1990 through 1992 using this procedure gave a mean recovery of 93% ± 10% at the 1-σ level. The data are published in Source Material 10.1 to 10.3.

3. Collection and Storage of Samples

3.1. QC samples are stored in volumetric flasks at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 500-mL, class A, glass.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Labels printed with QC sample numbers.

5. Reagents

5.1. Hydrochloric acid (concentrated, reagent-grade).

6. Calibration and Standards

6.1. When they are available, certified primary standards should be diluted to make a standard at the desired concentration.

6.2. Standard solutions that are not made from certified primary standards should be calibrated against an appropriate certified standard.

6.3. QC samples are spiked with a ^{90}Sr standard in 2 M HCl at a concentration of approximately 870 pCi/mL.

6.4. The ^{90}Sr standard should be calibrated against an Environmental Protection Agency (EPA)-certified ^{90}Sr standard solution in equilibrium with its daughter ^{90}Y.

6.5. Decay the ^{90}Sr standards each year.

6.5.1. The half-life of ^{90}Sr is 28.5 years.

6.5.2. The following equation describes the rate of radioactive decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms,
λ = the decay constant = $(\ln 2)/T_{1/2}$, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include 500 mL of 0.08 M HCl as a blank.

7.2. Add approximately 400 mL of distilled water to a 500-mL volumetric flask.

7.3. Add 3.5 mL of 12 M HCl to the water in the flask to produce 0.08 M acid.

7.4. Add an aliquot of ^{90}Sr standard to the water in the flask to reach the desired spike range.

7.5. Dilute the QC sample to volume with distilled water. Mix by inversion. Label the flask with a QC sample number, and store the flask at room temperature pending analysis.

7.6. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^{90}Sr in the QC sample as pCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 150 μL of a 870-pCi/mL ^{90}Sr standard is used to make a 500-mL QC sample, the ^{90}Sr concentration in the sample will be 261 pCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(870\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(150\ \mu\text{L})}{(500\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 261\ \frac{\text{pCi}}{\text{L}}$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box .

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.3. M. A. Gautier, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1992," Los Alamos National Laboratory report (in preparation).

10.4. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TRITIUM AND PERCENT MOISTURE ON SOIL — QC SAMPLE PREPARATION

Analyte: Tritium and percent moisture	**Method No.:** QCR250
Matrix: Sand	**Spike Range:** Tritium 80–400,000 pCi/L or 2–10,000 pCi/sample Percent moisture 2–5% H_2O
Procedure: Liquid scintillation counting and gravimetry	**Accuracy and Precision:** Tritium 100% ± 2.6% RSD Percent moisture 100% ± 9% RSD
Effective Date: 04/07/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.5 and 10.6 for proper waste disposal practices.

1. Principle of Method

1.1. Blank sand is aliquoted and spiked with a tritiated water standard.

1.2. Quality control (QC) samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. Propagated error for tritium.

2.1.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 2.6% at the 1-σ level has been calculated for the calibration and spiking process based on the following function:

$$D = M1 \times M2 \quad ,$$

where D = calculated result,
M1 = calibration error, and
M2 = spiking error.

2.1.2. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.3. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette, and
100 = factor to convert to percentage.

2.2. Propagated error for percent moisture.

2.2.1. The propagated error on QC preparation is based on the error associated with use of the analytical balance. An RSD of 9.0% has been calculated for the weighing process based on the following function:

$$D = \frac{M3}{M1 + M2} ,$$

where D = calculated result,
M3 = weighing error of water,
M1 = weighing error of first soil aliquot, and
M2 = weighing error of second soil aliquot.

2.2.2. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.2.3. Calculate percent RSD using the following equation.

$$SD_T = \frac{\sqrt{(R^2_{M3} + R^2_{M2})M2^2 + (R^2_{M3} + R^2_{M1})M1^2 + 2R^2_{M3}\ M1\ M2}}{(M1 + M2)} \times 100 ,$$

where SD_T = RSD (% error),
R^2_{M3} = relative variance of weight of water,
R^2_{M2} = relative variance of weight of second soil aliquot,
M2 = weight of second soil aliquot,
R^2_{M1} = relative variance of weight of first soil aliquot,
M1 = weight of first soil aliquot, and
100 = factor to convert to percentage.

2.3. Analysis by liquid scintillation counting of QC samples prepared from 1991 through 1993 using this procedure gave the following recoveries for tritium. Analysis by gravimetry of QC samples for percent moisture gave the following recoveries. The data are published in Source Materials 10.1. and 10.2.

TABLE I. ^3H AND PERCENT MOISTURE SPIKE RECOVERY DATA

Year	^3H	N	H_2O	N
1991	104 ± 13%	23	93 ± 5%	24
1992	101 ± 20%	60	84 ± 12%	10
1993	86 ± 15%	56	99 ± 15%	85

N = Number of samples.

3. Collection and Storage of Samples

3.1. QC samples are covered with plastic wrap and frozen pending analysis.

3.2. Data obtained in 1994 indicate that the QC samples are stable for at least five months if kept frozen until time of analysis.

4. Apparatus

4.1. Beakers: 1-L.

4.2. Pipettes: 10-, 15-, 20-, and 25-mL, class A volumetric.

4.3. Desiccator.

4.4. Drying oven: capable of reaching at least 110°C.

4.5. Spatula.

4.6. Plastic wrap.

4.7. Labels printed with QC sample numbers.

4.8. Balance: 1-kg minimum capacity, 0.1-g accuracy.

4.9. Jars: 1-L with Teflon-lined caps.

5. Reagents

5.1. Sand. A clean and dry 500-g aliquot is required for each sample.

5.2. A suitable sand does not contain the analyte of interest and presents few interferences to the analytical method.

6. Calibration and Standards

6.1. QC samples are spiked with tritium standards that contain ^{3}H in the concentration range 80 to 400,000 pCi/L.

6.2. A 25-mL aliquot of a ^{3}H standard in the concentration range 80 to 400,000 pCi/L spiked onto 500.0 g of clean, dry sand will produce a QC sample containing ^{3}H in the concentration range 2 to 10,000 pCi/sample and a total moisture content of approximately 5% by weight. The volume of water spiked onto the sand may vary between 10 and 25 mL but must be at least 10 mL.

6.3. Decay the ^{3}H standards each year.

6.3.1. The half-life of ^3H is 12.35 years.

6.3.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at desired time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = $(\ln 2)/T_{1/2}$ or the decay constant, where $T_{1/2}$ is the half-life.

6.4. The ^3H standard was calibrated against a National Institute of Standards and Technology (NIST)-certified ^3H Standard Reference Material (SRM), such as NIST SRM 4927B, a solution of tritiated water. Recalibrate the standard solution yearly by liquid scintillation counting.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. An aliquot of distilled water added to a soil sample may be included as a blank for ^3H analysis.

7.2. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of 500 g of sample in a 1-L glass jar.

7.3. Dry approximately 600 g of soil in a 1-L beaker at 105-110°C overnight.

7.4. Cool the soil in a desiccator.

7.5. Place a 1-L jar on a balance with a capacity of at least 1000 g. Tare the balance.

7.6. Add 300 g of soil to the jar. Record the weight and tare the balance.

7.7. Pipette 10 to 25 mL of tritium standard onto the center of the soil. Record the weight and tare the balance.

7.8. Add 200 g of soil to the jar to cover the wet soil, to bring the total soil weight to 500 ± 1 g and to achieve 2 to 5% H_2O. Record the final soil weight on the jar with a felt-tipped pen for reference by the analyst.

7.9. Label the jar with a QC sample number.

7.10. Cover the jar with plastic wrap, cap with Teflon-lined lid, and freeze pending analysis.

7.11. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the weight percent of extractable (unbound) water (H_2O^-) using the total sample weight (e.g., 500 g of soil plus 25 g of added H_2O).

8.2. Record the concentration of tritium as pCi/L. The tritium is measured as pCi/L and not as pCi/g because the determination measures the tritium concentration in the water in the sample and not the tritium concentration on the soil. Tritium concentration can be related to sample weight through the percent of H_2O^- in the sample.

8.3. Calculate the spike concentrations as in the following example.

8.3.1. If 25 mL of a 200,000-pCi/L tritium standard is used to spike 500.0 g of soil, the concentration of tritium in the sample is 200,000 pCi/L (5000 pCi/25 mL). Multiply the result by the RSD calculated in Step 2.1.1 to obtain the uncertainty.

$$(200{,}000 \text{ pCi/L})\ (1 \text{ L}/1000 \text{ mL})\ (25 \text{ mL}) = 5{,}000 \text{ pCi/sample} \quad .$$

8.3.2. The percent moisture is approximately 5% H_2O^-. Multiply the result by the RSD calculated in Step 2.2.1 to obtain the uncertainty.

$$\frac{(25 \text{ mL } H_2O)\ (1 \text{ g/mL}) \times 100}{500.0 \text{ g soil} + 25.0 \text{ g } H_2O} = 4.8\% \ H_2O \quad .$$

9. Proper Waste Disposal Practices

9.1. Solid waste.

9.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.1.3. Open the can only for the time necessary to add waste.

9.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.1.5. Put a new plastic bag into the waste can for continued use.

9.1.6. Place the sealed bag into a cardboard box lined with a plastic bag and keep the box inside a metal compactable waste container. On the sealed bag, reference the current Waste Profile Form (WPF) that describes the waste.

9.1.7. Label the metal container to indicate its use for radioactively contaminated waste.

9.1.8. When the cardboard box is full, seal the plastic bag liner and the box. Check the outside of the box for radioactive contamination and record the information in the Radioactive Waste Disposal logbook.

9.1.9. The radioactive solid waste coordinator marks the cardboard box as radioactively contaminated compactable waste and references the current WPF numbers describing the waste in the box on the outside of the box and in the Radioactive Waste Disposal logbook.

9.1.10. Place a new lined cardboard box into the metal container for continued use.

9.1.11. Place the sealed box in a dumpster for compactable mixed waste.

9.2. Liquid waste.

9.2.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.3. Waste pickup.

9.3.1. When the dumpster containing solid waste is full, the surface exposure rate of the dumpster is determined by a radiation control technician and is recorded on the Radioactive Solid Waste Disposal (RSWD) Record form.

9.3.2. On the RSWD, reference all the WPF numbers associated with the waste in the dumpster.

9.3.3. Request Waste Services (CST-17) to pick up a full dumpster. The RSWD and all the associated WPFs accompany the dumpster.

9.3.4. CST-17 disposes of the waste in accordance with Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory LA-12436-MS (1992).

10.2. M. A. Gautier, N. L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory LA-12790-MS (1994).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4927-B, Hydrogen-3" (National Institute of Standards and Technology, Washington, DC, January 1979).

10.4. M. P. Unterweger, B. M. Coursey, F. J. Schima, and W. B. Mann, "Preparation and Calibration of the 1978 National Bureau of Standards Tritiated-water Standards," *International Journal of Applied Radiation and Isotopes* **31**, 611-614 (1980).

10.5. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*," Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TRITIUM IN URINE — QC SAMPLE PREPARATION

Analyte: Tritium	**Method No.:** QCR260
Matrix: Urine	**Spike Range:** 0.0-10.0 μCi/L
Procedure: Liquid scintillation counting	**Accuracy and Precision:** 100% ± 3.7% RSD
Effective Date: 01/01/75	**Authors:** Margaret A. Gautier William D. Moss Nancy L. Koski

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.10 to 10.12 for proper waste disposal.

1. Principle of Method

1.1. A pool of blank urine is prepared.

1.2. The blank urine is aliquoted and spiked with a known standard.

1.3. Quality control (QC) samples are submitted for analysis with each routine analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error from six preparations of the standard and on the error associated with the use of the graduated cylinder and the pipette. A relative standard deviation (RSD) of 3.7% at the 1-σ level has been calculated for the calibration, spiking, and aliquoting process based on the following:

$$D = \frac{M1 \times M2}{M3 + M2} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = aliquoting error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = $M_1 \ldots M_n$ (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate the percent relative standard deviation using the following equation.

$$S_{D_T} = \sqrt{\frac{\left[R^2_{M1} (M_3 + M_2)^2 + M_3^2 (R^2_{M2} + R^2_{M3})\right]}{(M_3 + M_2)^2}} \times 100 ,$$

where S_{D_T} = relative standard deviation (% error),
R^2_{M1} = relative variance of standard,
M_3 = volume of cylinder,
M_2 = volume of pipette,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of cylinder, and
100 = factor to convert to percentage.

2.2. Analysis by liquid scintillation counting of QC samples prepared between 1984 and 1989 using this procedure gave a mean recovery of 98% ± 6% RSD. The data are published in Source Materials 10.1 through 10.6 and are summarized in Table I below.

TABLE I. TRITIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION

Year	Spike level (μCi/L)	Mean ± RSD (%)	Number of samples
1984	3.38	95 ± 9	15
	6.76	91 ± 3	12
	10.13	92 ± 3	10
	13.51	92 ± 4	7
	16.89	92 ± 2	5
1985	3.29	98 ± 4	22
	6.57	95 ± 3	19

TABLE I. TRITIUM SPIKE RECOVERY AS A FUNCTION OF CONCENTRATION (cont)

Year	Spike level (μCi/L)	Mean ± RSD (%)	Number of samples
1985	9.86	96 ± 5	15
	13.14	96 ± 2	12
	16.29	98 ± 2	9
1986	3.31	94 ± 3	22
	7.42	93 ± 4	22
	9.27	94 ± 3	18
	12.98	95 ± 3	16
	18.54	94 ± 4	18
1987	3.62	98 ± 6	34
	5.43	98 ± 7	38
	7.24	98 ± 5	39
	10.87	98 ± 5	27
1988	0.13	84 ± 23	16
	0.52	103 ± 10	41
	0.87	105 ± 8	41
	5.07	111 ± 8	41
	10.14	111 ± 7	39
1989	0.47	99 ± 14	27
	0.78	104 ± 14	27
	4.65	105 ± 14	28
	9.30	107 ± 13	26
	34.24	105 ± 14	25

3. Collection and Storage of Samples

3.1. Urine is collected as needed from group personnel who have no known contact with radiation work and is used to form a pool of blank urine.

3.2. Spiked QC samples are refrigerated at a nominal temperature of 4°C pending analysis.

4. Apparatus

4.1. Beakers: 4- or 5-L, polyethylene.

4.2. Graduated cylinders: 50-mL.

4.3. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.4. Pipette tips: disposable.

4.5. Specimen containers: 120-mL with screw caps, sterile inner surface, catalog no. C8845-3, Baxter Health Care Corp., Tempe, AZ 85282, or equivalent.

4.6. Labels printed with QC sample numbers.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. QC samples are spiked with tritium standards. The standards should be at a concentration of approximately 40 and 750 μCi/L.

6.2. Decay the tritium standard in January and July.

6.2.1. The half-life of tritium is 12.43 years.

6.2.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms,
λ = the decay constant = (ln 2)/$T_{1/2}$, where $T_{1/2}$ is the half-life.

6.3. The ^{3}H standard was calibrated against a National Institute of Standards and Technology (NIST)-certified ^{3}H solution of tritiated water, such as NIST Standard Reference Material (SRM) 4927B. Recalibrate the standard solution yearly by liquid scintillation counting. Record all data in the QC Laboratory notebook.

7. Procedure

7.1. Working with bodily fluids is discussed in detail in SOP-4, "Handling Human Biological Fluids and Tissues," found in Appendix III of the Environmental Chemistry Safety Manual.

NOTE: Wear safety glasses, gloves, and a lab coat. Each day prepare a 1:100 dilution of household bleach in water in a spray bottle. Use this solution to thoroughly clean the work area after sample preparation is completed. Remove gloves, discard them in the biohazard waste container, and wash hands with soap and water.

7.2. Prepare a pool of blank urine sufficient in volume to allow 50 mL for each QC sample to be prepared.

7.3. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Include blank QCs prepared from the same urine pool as the spiked samples. Tritium QC samples may be divided into two aliquots because only a 200-μL sample size is required by the analyst.

7.4. Record QC standard information, sample spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook.

7.5. Label bottles with QC sample numbers.

7.6. Aliquot 50 mL of blank urine into each sample bottle.

7.7. Spike the blank urine with aliquots of standard as determined in Step 7.3.

7.8. Screw caps on bottles and refrigerate at a nominal temperature of 4°C pending analysis.

7.9. Enter the spike concentration of each QC into the CVS and CVD databases on the VAX. This procedure is done annually because the same concentration levels are used throughout the year.

8. Calculations

8.1. Calculate spike concentration for a 300-μL aliquot of ^{3}H standard and report concentration as μCi/L using the following equation.

$$\frac{(750\ \mu\text{Ci/L})\ (\text{L}/1{,}000{,}000\ \mu\text{L})\ (300\ \mu\text{L})}{50\ \text{mL}\ (1\ \text{L}/1000\ \text{mL})} = 4.50\ \mu\text{Ci/L} \quad .$$

8.2. Spike concentrations calculated in Step 8.1 are tabulated below.

Concentration of standard (μCi/L)	Spike amount (μL)	QC concentration (pCi/sample)	Uncertainty (±3.7%)
—	0	0.00	0.00
40	600	0.48	0.02
40	1000	0.80	0.03
750	300	4.50	0.17
750	600	9.00	0.33

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Radiochemically contaminated waste.

9.2.1.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.1.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.1.3. Open the can only for the time necessary to add waste.

9.2.1.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.1.5. Put a new plastic bag into the waste can for continued use.

9.2.1.6. Place the sealed bag into a cardboard box lined with a plastic bag labeled to indicate its use for radioactively contaminated waste.

9.2.1.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.1.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.1.9. Line a new box with a plastic bag and label it for continued use.

9.2.1.10. Complete the current Radioactive Solid Waste Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.1.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.1.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.2.2. Biohazardous waste.

9.2.2.1. Dispose of bottles used to collect blank urine for a QC sample matrix as uncontaminated laboratory trash after they have been rinsed with dilute bleach solution.

9.2.2.2. Accumulate solid waste (such as paper wipes, plastic pipettes, and rubber gloves contaminated with biohazardous material, primarily urine) in a plastic bag labeled for the collection of biohazardous waste and keep it segregated from waste with no biohazard contamination.

9.2.2.3. Transfer full bags of biohazardous waste to a cardboard box labeled with a biohazard label and lined with a plastic bag bearing a biohazard label.

9.2.2.4. When the cardboard box is full, seal the liner bag and the box.

9.2.2.5. Line a new biohazard waste box with a plastic bag for further use.

9.3. Waste pickup.

9.3.1. Radiochemically contaminated waste.

9.3.1.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.1.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.2. Biohazardous waste.

9.3.2.1. Request CST-7 to pick up a full box of biohazardous waste using the current Chemical Waste Disposal Request (CWDR) form. The current WPF that describes the waste is referenced on the CWDR.

9.3.2.2. CST-7 arranges for pickup and disposal of the waste by the company currently under contract with the Laboratory for that purpose.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, and D. R. Perrin, "Quality Assurance for Health and Environmental Chemistry: 1984," Los Alamos National Laboratory report LA-10508-MS (1985).

10.2. M. A. Gautier, E. S. Gladney, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1985," Los Alamos National Laboratory report LA-10813-MS (1986).

10.3. M. A. Gautier, E. S. Gladney, W. D. Moss, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1986," Los Alamos National Laboratory report LA-11114-MS (1987).

10.4. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

10.5. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

10.6. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

10.7. M. P. Unterweger, B. M. Coursey, F. J. Schima, and W. B. Mann, "Preparation and Calibration of the 1978 National Bureau of Standards Tritiated-water Standards," *International Journal of Applied Radiation and Isotopes* 31, 611-614 (1980).

10.8. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4927-B, Hydrogen-3" (National Institute of Standards and Technology, Washington, DC, January 1979).

10.9. M. Phillips, "Handling Human Biological Fluids and Tissues," SOP-4, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Los Alamos National Laboratory document (November 1993).

10.10. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.11. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.12. "Managing Infectious Waste," Administrative Requirement 10-7, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒). Where a section heading is marked, the entire section has been revised.

TRITIUM IN WATER — QC SAMPLE PREPARATION

Analyte: Tritium	**Method No.:** QCR270
Matrix: Water	**Spike Range:** 10–20 nCi/L
Procedure: Liquid scintillation counting	**Accuracy and Precision:** 100% ± 3.7% RSD
Effective Date: 03/29/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 5. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.5 and 10.6 for proper waste disposal practices.

1. Principle of Method

1.1. A quality control (QC) sample for the determination of tritium in water is prepared by diluting a tritium standard to 10 mL with distilled water.

1.2. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standard and on the error associated with use of the pipette and of the volumetric flask. A relative standard deviation (RSD) of 3.7% at the 1-σ level has been calculated for the calibration, spiking, and dilution process based on the following function:

$$D = \frac{M1 \times M2}{M3} ,$$

where D = calculated result,
M1 = calibration error,
M2 = spiking error, and
M3 = dilution error.

2.1.1. Calculate relative variance using the following equation.

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1 . . . (variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.1.2. Calculate percent RSD using the following equation.

$$S_{D_T} = \sqrt{R_{M1}^2 + R_{M2}^2 + R_{M3}^2} \times 100 ,$$

where S_{D_T} = RSD (% error),
R^2_{M1} = relative variance of standard,
R^2_{M2} = relative variance of pipette,
R^2_{M3} = relative variance of volumetric flask, and
100 = factor to convert to percentage.

2.2. Analysis by liquid scintillation counting of QC samples from 1991 through 1993 using this procedure gave the following recoveries. The data are published in Source Materials 10.1 and 10.2.

TABLE I. TRITIUM IN WATER SPIKE RECOVERY DATA

Year	Mean ± std dev (%)	Number of Samples
1991	106 ± 20	176
1992	101 ± 15	157
1993	98 ± 11	138

3. Collection and Storage of Samples

3.1. QC samples are transferred to glass scintillation vials and are stored at room temperature pending analysis.

4. Apparatus

4.1. Volumetric flasks: 10-mL, Class A.

4.2. Auto-pipette: 100- and 1000-μL, Rainin or equivalent.

4.3. Pipette tips: disposable.

4.4. Graduated cylinder: 10-mL.

4.5. Scintillation vials: glass.

4.6. Parafilm.

4.7. Labels printed with QC sample numbers.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. When a certified primary standard is available, dilute it to make a standard at the desired concentration.

6.2. Calibrate standard solutions that are not made from certified primary standards against an appropriate certified standard.

6.3. Prepare QC samples by diluting a tritium standard to 10 mL with distilled water. The standard should be at a concentration of approximately 300 pCi/mL.

6.4. Calibrate the ^{3}H standard against a National Institute of Standards and Technology (NIST)-certified ^{3}H Standard Reference Material (SRM), such as NIST SRM 4927B, a solution of tritiated water. Recalibrate the standard solution annually by liquid scintillation counting and decay the ^{3}H concentration midway through the calibration period.

6.5. Decay the ^{3}H standards each year.

6.5.1. The half-life of ^{3}H is 12.35 years.

6.5.2. The following equation describes the rate of physical decay of radionuclides:

$$A_t = A_o e^{-\lambda t} ,$$

where A_t = the activity at time t,
A_o = the activity at t = 0,
e = the base of natural logarithms, and
λ = (ln 2)/$T_{1/2}$, the decay constant, where $T_{1/2}$ is the half-life.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. A 10-mL aliquot of distilled water may be included as a blank.

7.2. Sample size and container type may be varied to meet analytical requirements. This procedure describes the preparation of a 10-mL sample in a scintillation vial.

7.3. Preparation of QC blanks.

7.3.1. Prepare and seal QC blank samples before any tritium solutions are opened to avoid contamination of the blanks by tritiated water vapor.

7.3.2. Using a graduated cylinder, measure 10 mL of distilled water into a glass scintillation vial.

7.3.3. Cap the vial and wrap the cap with Parafilm.

7.3.4. Label the vial with a QC sample number.

7.3.5. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

7.4. Preparation of QC spiked samples.

7.4.1. Pour approximately 3 mL of distilled water into a 10-mL volumetric flask.

7.4.2. Pipette an aliquot of the tritium standard solution into the flask to reach the desired spike range.

7.4.3. Dilute the standard to volume with distilled water. Mix by inverting.

7.4.4. Transfer the standard from the flask to a glass scintillation vial.

7.4.5. Cap the vial and wrap the cap with Parafilm.

7.4.6. Label the vial with a QC sample number.

7.4.7. Record QC standard information, sample number, sample description, spike amount, concentration, uncertainty, and all calculations in the QC Laboratory notebook and in the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the concentration of ^3H in the water as pCi/L or nCi/L.

8.2. Calculate spike concentrations as in the following example.

8.2.1. If 400 μL of a 300-pCi/L tritium standard is used to spike a 10-mL QC sample, the concentration of tritium in the sample is 12 nCi/L. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{\left(300\ \frac{\text{pCi}}{\text{mL}}\right)\left(\frac{1\ \text{mL}}{1000\ \mu\text{L}}\right)(400\ \mu\text{L})\left(\frac{1\ \text{nCi}}{1000\ \text{pCi}}\right)}{(10.0\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 12\ \text{nCi/L} \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Services (CST-17) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-17, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1 M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

10.2 M. A. Gautier, N.L. Koski, and E. A. Jones, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1994).

10.3. National Institute of Standards and Technology, "Certificate of Analysis for Standard Reference Material 4927-B, Hydrogen-3" (National Institute of Standards and Technology, Washington, DC, January 1979).

10.4. M. P. Unterweger, B. M. Coursey, F. J. Schima, and W. B. Mann, "Preparation and Calibration of the 1978 National Bureau of Standards Tritiated-water Standards," *International Journal of Applied Radiation and Isotopes* 31, 611-614 (1980).

10.5. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

URANIUM IN SOIL — QC SAMPLE PREPARATION

Analyte: Uranium	**Method No.:** QCR280
Matrix: Soil	**Spike Range:** 10-500 μg/g
Procedure: Delayed neutron activation	**Accuracy and Precision:** 100% ± 3.3% RSD
Effective Date: 08/09/89	**Authors:** Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the standards listed in Sec. 6. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 9 of this procedure and Source Materials 10.5 and 10.6 for proper waste disposal practices.

1. Principle of Method

1.1. Two soils with certified uranium contents are combined in varying proportions to make quality control (QC) samples with uranium concentrations in the desired spike range.

1.2. No soils tested had a sufficiently low and consistent uranium background to allow use as a blank sample or as a soil sample matrix.

1.3. QC samples are submitted for analysis with each analytical batch and are analyzed along with the unknown samples using the same analytical procedure.

2. Accuracy and Precision

2.1. The propagated error on QC preparation is based on the calibration error of the standards and on the error associated with use of the analytical balance. A relative standard deviation (RSD) of 3.3% at the 1-σ level has been calculated for the calibration and spiking process based on the following function:

$$D = \frac{M1\ M3 + M2\ M4}{M3 + M4} ,$$

where D = calculated result,
M1 = calibration error of standard one,
M2 = calibration error of standard two,
M3 = weighing error of standard one, and
M4 = weighing error of standard two.

2.2. Calculate relative variance using the following equation:

$$R_M^2 = \frac{\sigma^2}{\overline{X}^2} ,$$

where R^2_M = relative variance,
M = M1. . .(variable),
σ^2 = variance (std dev^2), and
$\overline{X}$ = mean value of each variable (M).

2.3. Calculate percent RSD using the following equation:

$$S_{D_T} = \sqrt{A + B} \times 100 ,$$

where

$$A = \frac{(R^2_{M3} + R^2_{M4})\,(M2 - M1)^2\, M3^2\, M4^2}{(M3 + M4)^2\,(M2\,M4 + M1\,M3)^2} ,$$

$$B = \frac{R^2_{M2}\, M2^2\, M4^2 + R^2_{M1}\, M1^2\, M3^2}{(M2\,M4 + M1\,M3)^2} ,$$

SD_T = RSD (% error),
R^2_{M3} = relative variance of standard weight one,
R^2_{M4} = relative variance of standard weight two,
M2 = calibration error of standard two,
M1 = calibration error of standard one,
M3 = weighing error of standard one,
M4 = weighing error of standard two,
R^2_{M2} = relative variance of standard two,
R^2_{M1} = relative variance of standard one, and
100 = factor to convert to percentage.

2.4. Analysis by delayed neutron activation of QC samples prepared during 1989 and 1990 using this procedure gave a mean recovery of 94% ± 2% RSD. The data are published in Source Materials 10.1 and 10.2 and are summarized Table I below.

TABLE I. URANIUM SPIKE RECOVERY DURING 1989 AND 1990 AS A FUNCTION OF CONCENTRATION		
Spike range, μg/g	Mean ± RSD (%)	Number of samples
10 — 50	95 ± 4	4
50 — 100	95 ± 1	4
150 — 200	94 ± 1	3
200 — 250	94 ± 1	5

3. Collection and Storage of Samples

3.1. QC samples are stored in polyethylene reactor rabbits at room temperature pending analysis.

4. Apparatus

4.1. Reactor rabbits: polyethylene, to contain soil samples during irradiation in the reactor.

4.2. Commercial canned dust-chaser spray.

4.3. Spatulas.

4.4. Analytical balance: 100-g capacity, 0.1-mg accuracy.

4.5. Labels printed with QC sample numbers.

5. Reagents

5.1. None required.

6. Calibration and Standards

6.1. The total weight of soil in each reactor rabbit is 1.0000 g.

6.2. Select two soils with consensus or certified uranium concentrations, one near the lower limit and the other near the upper limit of the desired concentration range. Two such soils are Canadian Certified Reference Materials Project (CCRMP) SO-3, Calcareous C Uranium Soil, with a certified uranium concentration of 1.11 ± 0.02 μg/g, and CCRMP SY-2, Syenite, with a certified uranium concentration of 284 ± 9 μg/g.

6.3. One certified soil may be used alone or combined with a second certified soil to make a QC sample with a uranium concentration in the desired spike range.

7. Procedure

7.1. Prepare QC samples to equal at least 10% of the total number of samples to be analyzed. Periodically include an unspiked sample as a blank.

7.2. Place a polyethylene rabbit on the balance. Tare the balance.

7.3. To prepare a QC sample with the same uranium concentration as the certified soil, accurately weigh 1.0000 g of the certified soil into the reactor rabbit. Clean the rabbit threads before recording the soil weight.

NOTE: The threads on the polyethylene reactor rabbit must be free of any soil residue before closing to prevent the rabbit from opening during irradiation. Use a commercial canned dust-chaser spray to blow the rabbit threads free of any soil before determining the final weight of soil added and capping the rabbit.

7.4. To prepare a QC sample with a uranium concentration different from the concentration in either of the two certified soils, determine a suitable ratio in which to mix the two certified soils to obtain a uranium concentration in the desired spike range and a total sample weight of 1.0000 g.

NOTE: When mixing two soils, weigh out at least 30 mg (0.03 g) of each soil to remain within the calculated RSD in Step 2.1.

7.4.1. Weigh an aliquot of the first soil into the reactor rabbit. Clean the rabbit threads. Record the soil weight and tare the balance.

7.4.2. Weigh an aliquot of the second soil into the reactor rabbit. Clean the rabbit threads before recording the soil weight.

7.5. Cap the reactor rabbit, making certain no residual soil remains on the threads.

7.7. Mix the two soils in the QC sample by shaking the rabbit.

7.8. Do not place a sample label on the rabbit because it will interfere with the free movement of the rabbit in and out of the reactor. Use a pen to write a QC number on the reactor rabbit. Destroy the associated printed sample label. Record the total sample weight on the rabbit for reference by the analyst.

7.9. Record QC standard information, sample number, sample description, certified soil weights, uranium concentrations, uncertainty, and all calculations in the QC Laboratory notebook and enter into the CVS and CVD databases on the VAX.

8. Calculations

8.1. Record the final concentration of uranium in the soil as $\mu g/g$.

8.2. Calculate final uranium concentration as in the following example.

8.2.1. If 0.7951 g of CCRMP SO-3, Calcareous C Uranium Soil, with a uranium concentration of 1.11 ± 0.02 $\mu g/g$, and 0.2646 g of CCRMP SY-2, Syenite, with a uranium concentration of 284 ± 9 $\mu g/g$, are combined in a reactor rabbit, the QC sample will have a final weight of 1.0597 g and a uranium concentration of 72 $\mu g/g$. Multiply the result by the RSD calculated in Step 2.1 to obtain the uncertainty.

$$\frac{(0.7951\ g)\ (1.11\ \mu g/g)\ +\ (0.2646\ g)\ (284\ \mu g/g)}{0.7951\ g\ +\ 0.2646\ g} = 72\ \mu g/g \quad .$$

9. Proper Waste Disposal Practices

9.1. Liquid waste.

9.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

9.2. Solid waste.

9.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

9.2.2. Label the can to indicate its use for radioactively contaminated waste.

9.2.3. Open the can only for the time necessary to add waste.

9.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

9.2.5. Put a new plastic bag into the waste can for continued use.

9.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labelled to indicate its use for radioactively contaminated waste.

9.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

9.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

9.2.9. Line a new box with a plastic bag and label it for continued use.

9.2.10. Complete the current Radioactive Solid Waste Disposal Record (RSWD) form describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

9.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

9.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

9.3. Waste pickup.

9.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of waste.

9.3.2. The RSWD and a copy of the associated WPF accompany the full box.

9.3.3. The waste is disposed of according to Laboratory policy.

10. Source Materials

10.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory LA-11995-MS (1990).

10.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory LA-12208-MS (1991).

10.3. Canada Centre for Mineral and Energy Technology, "Certificate of Analysis for Reference Soil Sample SO-3" (Canada Centre for Mineral and Energy Technology, Ottowa, Ontario, Canada, 1985).

10.4. Canada Centre for Mineral and Energy Technology, "Certificate of Analysis for Reference Soil Sample SY-2" (Canada Centre for Mineral and Energy Technology, Ottowa, Ontario, Canada, December 1979).

10.5. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

10.6. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

Revisions or additions to the procedure are marked (▒▒▒▒). Where a section heading is marked, the entire section has been revised.

PREPARATION OF A VEGETATION ASH MATRIX

Analyte: None	**Method No.:** QCM200
Procedure: Ashing of vegetation	
Effective Date: 11/29/90	**Authors:** Bennie A. Martinez Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 3. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 5 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. Vegetable matter is ashed slowly to create a vegetation ash suitable for use as a blank matrix for quality control (QC) samples.

2. Apparatus

2.1. Beakers: 1-L, glass.

2.2. Aluminum foil.

2.3. Balance: 1-kg minimum capacity, 0.1-g accuracy.

2.4. Muffle furnace capable of reaching and sustaining a temperature of at least 550°C.

2.5. Engraver.

2.6. Bottle: 1-gal. capacity or smaller.

2.7. Sieve: No. 18

2.8. Ball mill and polyethylene container, with lid, for ball mill.

2.9. Steel balls: 5/8- to 3/4-in. diameter.

2.10. Vinyl tape.

2.11. Spatula.

2.12. Insulated gloves.

3. Reagents

3.1. Chicken Scratch containing no additives or an equivalent vegetation feed may provide a suitable ash.

3.2. A suitable vegetation ash does not contain the analyte of interest and presents few interferences to the analytical method.

4. Procedure

4.1. The muffle furnace should be equipped with a safety switch that shuts the furnace off in case the temperature exceeds its setting. It should also be vented or located where fumes will not contaminate working spaces.

4.2. Weigh approximately 500 g of chicken feed into a 1-L beaker.

4.3. Dry the feed in a muffle furnace at 100°C for about 48 h.

4.4. Cover the beaker with aluminum foil perforated with 1/4- to 1/2-in. holes and place the covered beaker in the muffle furnace. Several beakers of feed may be ashed simultaneously, considering the capacity of the furnace.

4.5. Ash the feed by raising the temperature of the muffle furnace slowly from 150°C to 550°C over an 80-h period. Be especially cautious to raise the temperature slowly between 225°C and 325°C, the range in which the feed is most likely to ignite spontaneously. Most of the odor from the ashing process should occur below 450°C.

4.6. Maintain the muffle furnace at 550°C for 7 days.

4.7. Turn off the furnace and allow the sample to cool until the beaker can be safely handled, about 6 h.

4.8. Remove the beaker from the furnace and transfer the ash to the ball mill container. Fill the container no more than half full and add about 100 steel balls. Cap the container and seal it with tape.

4.9. Place the container on the ball mill and grind the ash for about 1 h.

4.10. Allow the ash to settle before opening the container.

4.11. Sift the ash through a No. 18 sieve. Using a spatula, transfer the ash that passes through the sieve to a storage bottle and place the rest back into the ball mill

container. Repeat the grinding and sifting until all the ash has been ground and sifted.

4.12. Re-ash the matrix to constant weight.

4.12.1. Fill a 1-L beaker, engraved with an identifying number, approximately half full with sifted ash. Cover the beaker with aluminum foil perforated with 1/4- to 1/2-in. holes.

4.12.2. Weigh the covered beaker and ash. Record the weight in a Laboratory notebook. Several beakers of ash may be re-ashed simultaneously, considering the capacity of the furnace.

4.12.3. Re-ash the feed by raising the temperature of the muffle furnace slowly from 250°C to 550°C over 8 h.

4.12.4. Maintain the muffle furnace at 550°C for 3 days.

4.12.5. Turn off the furnace and allow the ash to cool for approximately 6 h.

4.12.6. Weigh the covered beaker and ash. Record the weight and compare it with the previously recorded weight. If there has been no significant change and the ash is gray, no further ashing is necessary.

4.12.7. If there has been a significant change in weight or if the ash is not gray in color, re-ash the feed at 550°C for about 36 h. Continue weighing and re-ashing until the ash is gray and at a constant weight.

5. Proper Waste Disposal Practices

5.1. No waste is produced.

6. Source Materials

6.1. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

6.2. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

6.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

6.4. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report LA-12790-MS (1993).

Revisions or additions to the procedure are marked (). Where a section heading is marked, the entire section has been revised.

EPA AIR FILTER PERFORMANCE EVALUATION STUDY

Analyte: Alpha, beta, ^{90}Sr, and ^{137}Cs	**Method No.:** QCS100
Matrix: Air filter	
Procedure: Proportional counting for alpha and beta; gamma spectroscopy for ^{137}Cs; radiochemical alpha spectrometry for ^{90}Sr	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits air filter performance evaluation samples for alpha, beta, ^{90}Sr, and ^{137}Cs analysis.

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is required.

2.2. Samples are sealed with chain-of-custody tape and stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Samples are received in individual filter cases.

5.2. Seal each case with chain-of-custody tape.

5.3. Label the cases with a QC sample number. The same QC sample number may be used for replicate samples.

5.4. Store the samples at room temperature pending analysis.

5.5. Distribute a copy of the EPA reporting sheet with the samples.

5.6. Record on the copy of the EPA reporting sheet distributed to the analyst that ^{137}Cs by gamma spectroscopy MUST be completed before the filters are digested for the other analyses.

5.7. Submit one QC sample (NEVER A BLANK), where available, matching the matrix of the performance evaluation sample.

5.8. Establish a due date for the study, allowing sufficient time to record and mail the data to EPA to meet their stated deadline.

5.9. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.10. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

DOE BERYLLIUM INTERCOMPARISON STUDY PROCEDURE

Analyte: Beryllium	**Method No.:** QCS110
Matrix: Filters	
Procedure: Inductively coupled plasma-atomic emission spectroscopy	
Effective Date: 01/01/87	**Authors:** Rebecca Eaton Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. Filter media intercomparison samples for beryllium analysis are prepared and distributed by Oak Ridge National Laboratory.

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is necessary.

2.2. Samples are labeled, sealed with chain-of-custody tape, and stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Samples are received in individual filter cases.

5.2. Seal each case with chain-of-custody tape.

5.3. Label each case with a QC sample number.

5.4. Store the samples at room temperature pending analysis.

5.5. Distribute a copy of the reporting sheet and procedure information request sheet with the samples.

5.6. Submit QC samples, prepared as described in Method No. QCI140, "Trace Elements on Filter Media-QC Sample Preparation," along with the intercomparison samples.

5.7. Establish a Quality Assurance and Data Management (QADM) section due date allowing sufficient time to record and mail the sample intercomparison data by the stated deadline.

5.8. Record the Intercomparison study identity, agency, sample numbers, sample descriptions, analyses requested, date received, due date, and matrix in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and in the CVD database on the VAX.

5.9. Deliver all study samples, QC samples, and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the intercomparison study report sheet, making sure the reported units match those requested by the study.

6.2. Send the completed report form to the sample submitter by the required deadline.

6.3. Record in the External Quality Assurance Samples notebook the results and the date the report was sent.

7. Intercomparison Certified Values

7.1. When the certified study sample values are received from Oak Ridge National Laboratory, enter the values on the samples data sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, symbol (if appropriate), certified values and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the QADM files and send a copy of the report to the section leader of the section which performed the analyses.

8. Proper Waste Disposal Practices

8.1. No waste is generated by this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.2. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.5. M. A. Gautier, E. A. Jones, and N. L. Koski, "Quality Assurance for Environmental Chemistry: 1992," Los Alamos National Laboratory report (in preparation).

EPA GAMMA IN WATER PERFORMANCE EVALUATION STUDY

Analyte: ^{60}Co, ^{65}Zn, ^{106}Ru, ^{134}Cs, ^{137}Cs, and ^{133}Ba	**Method No.:** QCS130
Matrix: Water	
Procedure: Gamma spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.6 and 9.7 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for ^{60}Cs, ^{65}Zn, ^{106}Ru, ^{134}Cs, ^{137}Cs, and ^{133}Ba analysis. Samples are diluted according to supplied instructions.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate as 500-mL aliquots in 500-mL polyethylene bottles sealed with chain-of-custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 100-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Bottles: 500-mL, high-density polyethylene.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Chain-of-custody tape.

3.9. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of a 2-L aliquot.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL sample aliquot to 2 L.

5.2. Prepare 2 L of 0.5 M hydrochloric acid.

5.2.1. Put approximately 1900 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2. Add 85.5 mL of 12 M HCl to the water, using a 100-mL graduated cylinder.

5.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.4. Mix the acid with a long stirring rod.

5.3. Transfer a 250-mL aliquot of the performance evaluation sample to a 2-L volumetric flask, using a 250-mL graduated cylinder.

5.4. Dilute the sample to volume with 0.5 M HCl.

5.5. Mix by inversion.

5.6. Pour the 2-L sample aliquot into a 5-L beaker and set it on a stirring plate.

5.7. Place a Teflon-coated stirring bar in the beaker and stir the solution slowly for 20-30 min.

5.8. Using a graduated cylinder, measure 500-mL aliquots into each of three 500-mL high-density polyethylene bottles.

5.9. Dispose of excess sample as radioactively contaminated liquid waste.

5.10. Cap the bottles and seal with chain-of-custody tape.

5.11. Label each bottle with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.12. Write the sample collection date on the label for reference by the analyst.

5.13. Include one QC sample (NEVER A BLANK) prepared as described in Method No. QCR130, Cesium-137 in Water—QC Sample Preparation.

5.14. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.15. Establish a due date for the analysis, allowing sufficient time to record and mail the data to EPA to meet their stated deadline.

5.16. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.17. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results, and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of liquid radioactively contaminated waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EPA BLIND A AND B PERFORMANCE EVALUATION STUDY

Analyte: Sample A: gross alpha, ^{226}Ra, and U Sample B: gross beta, ^{90}Sr, ^{134}Cs, ^{137}Cs, and ^{60}Co	**Method No.:** QCS150
Matrix: Water	
Procedure: Proportional counting for gross alpha and gross beta; gamma spectroscopy for ^{134}Cs, ^{137}Cs, and ^{60}Co; radiochemical alpha spectrometry for ^{90}Sr and ^{226}Ra; and inductively coupled plasma-mass spectrometry (ICPMS) for U	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.6 and 9.7 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits two water performance evaluation samples. Sample A includes analyses for gross alpha, ^{226}Ra, ^{228}Ra, and U. Sample B includes analyses for gross beta, ^{89}Sr, ^{90}Sr, ^{134}Cs, ^{137}Cs, and ^{60}Co. Samples are diluted according to supplied instructions.

1.2. Environmental Chemistry (CST-9) does not analyze for ^{228}Ra and ^{89}Sr.

2. Collection and Storage of Samples

2.1. Triplicate 900-mL aliquots for gross alpha, ^{226}Ra, and gross beta analyses are distributed in 1000-mL beakers. The beakers are covered with plastic wrap and sealed with chain-of-custody tape.

2.2. Triplicate 500-mL aliquots for ^{90}Sr analysis are distributed in 600-mL beakers. The beakers are covered with plastic wrap and sealed with chain-of-custody tape.

2.3. Triplicate 100-mL aliquots for U analysis are distributed in 125-mL polyethylene bottles. The bottles are sealed with chain-of-custody tape.

2.4. One 1-L aliquot for ^{134}Cs, ^{137}Cs, and ^{60}Co analysis is distributed in a 1-L Marinelli beaker. The beaker is sealed with chain-of-custody tape.

2.5. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 25-, 250-, 500-, 1000-, 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beaker: 1-L, polyethylene Marinelli.

3.5. Beakers: 600- and 1000-mL, glass.

3.6. Bottles: 125-mL, high-density polyethylene.

3.7. Long glass stirring rod.

3.8. Teflon-coated magnetic stirring bars.

3.9. Magnetic stirring plate.

3.10. Plastic wrap.

3.11. Chain-of-custody tape.

3.12. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. Nitric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4L, aliquot of diluted sample.

5.1.1. This procedure describes preparation of three 2-L aliquots.

5.1.2. If EPA instructions call for dilution of a 250-mL sample aliquot to 4 L the same dilution is achieved by diluting a 125-mL sample aliquot to 2 L.

5.2. Preparation of the 2-L aliquots of sample A.

5.2.1. Add a Teflon-coated stirring bar to the 1-quart container of concentrated sample A and stir the solution for approximately 10 min to redissolve any precipitates and ensure homogeneity of the sample.

5.2.2. Prepare 2 L of 0.1 M nitric acid.

5.2.2.1. Put approximately 1950 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2.2. Add 12.8 mL of 16 M HNO_3 to the water, using a 25-mL graduated cylinder.

5.2.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.2.4. Mix the acid with a long glass stirring rod.

5.2.3. Transfer a 125-mL aliquot of performance evaluation sample A into a 2-L volumetric flask using a 250-mL graduated cylinder.

5.2.4. Dilute the sample to volume with 0.1 M HNO_3.

5.2.5. Mix by inversion.

5.2.6. Pour the 2-L sample aliquot into a 5-L beaker.

5.2.7. Repeat Steps 5.2.2 through 5.2.5.

5.2.8. Combine the second 2-L sample aliquot with the first and set the beaker on a stirring plate.

5.2.9. Place a Teflon-coated stirring bar in the beaker and stir the solution slowly for approximately 10 min.

5.2.10. Using a graduated cylinder, measure 900-mL aliquots into each of three 1000-mL beakers for gross alpha analysis.

5.2.11. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.2.12. Repeat Steps 5.2.2 through 5.2.5.

5.2.13. Combine the additional 2-L sample with the sample remaining in the 5-L beaker.

5.2.14. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.2.15. Using a graduated cylinder, measure 900-mL aliquots into each of three 1000-mL beakers for ^{226}Ra analysis.

5.2.16. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.2.17. Using a graduated cylinder, measure 100-mL aliquots into each of three 125-mL polyethylene bottles for U analysis.

5.2.18. Seal each bottle with chain-of-custody tape.

5.2.19. Dispose of the excess sample as radioactively contaminated liquid waste.

5.3. Preparation of the 2-L aliquots of sample B.

5.3.1. Add a Teflon-coated stirring bar to the 1-quart container of concentrated sample B and stir the solution for approximately 10 min to redissolve any precipitates and ensure homogeneity of the sample.

5.3.2. Prepare 2 L of 0.1 M nitric acid.

5.3.2.1 Put approximately 1950 mL of distilled water into a 2000-mL graduated cylinder.

5.3.2.2. Add 12.8 mL of 16 M HNO_3 to the water, using a 25-mL graduated cylinder.

5.3.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.3.2.4. Mix the acid with a long glass stirring rod.

5.3.3. Transfer a 125-mL aliquot of performance evaluation sample B into a 2-L volumetric flask using a 250-mL graduated cylinder.

5.3.4. Dilute the sample to volume with 0.1 M HNO_3.

5.3.5. Mix by inversion.

5.3.6. Pour the 2-L sample aliquot into a 5-L beaker.

5.3.7. Repeat Steps 5.3.2 through 5.3.5.

5.3.8. Combine the second 2-L sample aliquot with the first and set the beaker on a stirring plate.

5.3.9. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.3.10. Using a graduated cylinder, measure 900-mL aliquots into each of three 1000-mL beakers for gross beta analysis.

5.3.11. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.3.12. Repeat Steps 5.3.2 through 5.3.5.

5.3.13. Combine the additional 2 L of sample with the sample remaining in the 5-L beaker.

5.3.14. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 10 min.

5.3.15. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers for ^{90}Sr analysis.

5.3.16. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.3.17. Measure a 1-L aliquot using a graduated cylinder into a 1-L Marinelli beaker for ^{134}Cs, ^{137}Cs, and ^{60}Co analysis.

5.3.18. Seal the Marinelli beaker with chain-of-custody tape.

5.3.19. Dispose of excess sample as radioactively contaminated liquid waste.

5.4. Label each beaker and bottle with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.5. Include QC samples (NEVER A BLANK) prepared as described in the following methods: QCR150, Gross Alpha and Gross Beta in Water—QC Sample Preparation; QCR130, Cesium-137 in Water—QC Sample Preparation; QCR220, Radium-226 in Water—QC Sample Preparation; QCR240, Strontium-90 in Water—QC Sample Preparation; and QCI170, Trace Elements in Nitric Acid—QC Sample Preparation, for natural uranium analysis by ICPMS.

5.6. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.7. Establish a due date for the analyses, allowing sufficient time to record and mail data to EPA to meet their stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analyses requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.9. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of liquid radioactively contaminated waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactive contaminated waste.

8.2.3. Open the can only for the period of time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EPA PLUTONIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Plutonium	**Method No.:** QCS180
Matrix: Water	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.6 and 9.7 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for ^{239}Pu analysis. Samples are diluted according to supplied instructions.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate 300-mL and 500-mL aliquots for analysis by the Radiochemistry section, using tissue, bioassay, and environmental analytical procedures.

2.2. Samples are sealed with chain-of-custody tape and stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 25-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 400- and 600-mL, glass.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Plastic wrap.

3.9. Chain-of-custody tape.

3.10. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of two 2-L aliquots.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL sample aliquot to 2 L.

5.2. Prepare 2 L of 3 M hydrochloric acid.

5.2.1. Put approximately 1400 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2. Add 513 mL of 12 M HCl to the water using a 500-mL and a 25-mL graduated cylinder.

5.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.4. Mix the acid with a long stirring rod.

5.3. Transfer a 250-mL aliquot of the performance evaluation sample into a 2-L volumetric flask using a 250-mL graduated cylinder.

5.4. Dilute the sample to volume with 3 M HCl.

5.5. Mix by inversion.

5.6. Pour the 2-L sample aliquot into a 5-L beaker.

5.7. Repeat Steps 5.2 through 5.5.

5.8. Combine the second 2-L sample aliquot with the first and set the beaker on a stirring plate.

5.9. Place a Teflon-coated stirring bar in the beaker and slowly stir the solution for approximately 5 min.

5.10. Using a graduated cylinder, measure 300-mL aliquots into each of three 400-mL beakers for analysis using the tissue analytical procedure for Pu (Method No. RT500).

5.11. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers for analysis using the environmental analytical procedure for Pu (Method No. ER160).

5.12. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers for analysis using the bioassay analytical procedure for Pu (Method No. R170).

5.13. Dispose of excess sample as radioactively contaminated liquid waste.

5.14. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.15. Label each beaker with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.16. Include three QC samples (NEVER A BLANK) prepared as described Method No. QCR180, Plutonium and Americium in Water—QC Sample Preparation.

5.17. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.18. Establish a due date for the analysis, allowing sufficient time to record and mail the data to EPA to meet their stated deadline.

5.19. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.20. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactively contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EPA RADIONUCLIDES IN MILK PERFORMANCE EVALUATION STUDY

Analyte: ^{90}Sr	**Method No.:** QCS200
Matrix: Biological	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.6 and 9.7 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits performance evaluation samples for ^{131}I, ^{137}Cs, ^{40}K, ^{90}Sr, and ^{89}Sr analysis. Samples are diluted according to supplied instructions.

1.2. Environmental Chemistry (CST-9) does not analyze for ^{131}I, ^{137}Cs, ^{40}K and ^{89}Sr.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate as 500-mL aliquots in 600-mL beakers covered with plastic wrap and sealed with chain-of-custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Graduated cylinder: 500-mL.

3.2. Beakers: 600-mL, glass.

3.3. Plastic wrap.

3.4. Chain-of-custody tape.

3.5. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers.

5.2. Reserve excess sample until analysis is completed then dispose of it as radioactively contaminated liquid waste.

5.3. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.4. Label each beaker with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.5. Include one QC sample (NEVER A BLANK) prepared as described in Method No. QCR240, Strontium in Water—QC Sample Preparation.

5.6. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.7. Establish a due date for the analysis, allowing sufficient time to record and mail the data to EPA to meet their stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.9. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA result sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EPA RADIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Radium-226	**Method No.:** QCS210
Matrix: Water	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/85 to 01/01/94	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the Material Safety Data Sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.6 and 9.7 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water intercomparison samples for Ra-226 and Ra-228 analysis. Samples are diluted according to supplied instructions.

1.2. Ra-228 is not analyzed for by CST-9.

2. Collection and Storage of Samples

2.1. Intercomparison samples are distributed in triplicate as 900-mL aliquots in 1000-mL beakers covered with plastic wrap and sealed with chain of custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flasks: 1- and 2-L, class A, glass.

3.2. Graduated cylinders: 100-, 250-, 1000-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 1000-mL, glass.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Plastic wrap.

3.9. Chain of custody tape.

3.10. Labels printed with QC sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of one 2-L and one 1-L aliquot.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL aliquot to 2 L or a 125-mL aliquot to 1 L.

5.2. Preparation of the 2-L aliquot.

5.2.1. Prepare 2 L of 0.5 M hydrochloric acid.

5.2.1.1. Put approximately 1900 mL of distilled water into a 2000-mL graduated cylinder.

5.2.1.2. Add 85.5 mL of 12 M HCl to the water, using a 100-mL graduated cylinder.

5.2.1.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.1.4. Mix the acid with a long stirring rod.

5.2.2. Transfer a 250-mL aliquot of the intercomparison sample into a 2-L volumetric flask, using a 250-mL graduated cylinder.

5.2.3. Dilute the sample to volume with 0.5 M HCl.

5.2.4. Mix by inversion.

EPA STRONTIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: ^{90}Sr	**Method No.:** QCS220
Matrix: Water	
Procedure: Radiochemical alpha spectrometry	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure and Source Materials 9.6 and 9.7 for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for ^{89}Sr and ^{90}Sr analysis. Samples are diluted according to supplied instruction.

1.2. Environmental Chemistry (CST-9) does not analyze for ^{89}Sr.

2. Collection and Storage of Samples

2.1. Performance evaluation samples are distributed in triplicate as 500-mL aliquots in 600-mL beakers covered with plastic wrap and sealed with chain-of-custody tape.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Volumetric flask: 2-L, class A, glass.

3.2. Graduated cylinders: 100-, 250-, 500-, and 2000-mL.

3.3. Beaker: 5-L, polyethylene.

3.4. Beakers: 600-mL, glass.

3.5. Long glass stirring rod.

3.6. Teflon-coated magnetic stirring bar.

3.7. Magnetic stirring plate.

3.8. Plastic wrap.

3.9. Chain-of-custody tape.

3.10. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. Hydrochloric acid (concentrated, reagent-grade).

5. Procedure

5.1. EPA instructions specify preparation of a 4-L aliquot of diluted sample.

5.1.1. This procedure describes preparation of one 2-L aliquot.

5.1.2. If EPA instructions call for dilution of a 500-mL sample aliquot to 4 L, the same dilution is achieved by diluting a 250-mL sample aliquot to 2 L.

5.2. Prepare 2 L of 0.5 M hydrochloric acid.

5.2.1. Put approximately 1900 mL of distilled water into a 2000-mL graduated cylinder.

5.2.2. Add 85.5 mL of 12 M HCl to the water, using a 100-mL graduated cylinder.

5.2.3. Allow the acid to cool and dilute to 2000 mL with distilled water.

5.2.4. Mix the acid with a long stirring rod.

5.3. Transfer a 250-mL aliquot of the performance evaluation sample into a 2-L volumetric flask, using a 250-mL graduated cylinder.

5.4. Dilute the sample to volume with 0.5 M HCl.

5.5. Mix by inversion.

5.6. Pour the 2-L sample aliquot into a 5-L beaker and set it on a stirring plate.

5.7. Place a Teflon-coated stirring bar in the beaker and stir the solution slowly for 20-30 min.

5.8. Using a graduated cylinder, measure 500-mL aliquots into each of three 600-mL beakers.

5.9. Dispose of excess sample as radioactively contaminated liquid waste.

5.10. Cover each beaker with plastic wrap and seal with chain-of-custody tape.

5.11. Label each beaker with a QC sample number and store the samples at room temperature pending analysis. The same QC sample number may be used for replicate aliquots.

5.12. Include one QC sample (NEVER A BLANK) prepared as described in Method No. QCR240, Strontium-90 in Water—QC Sample Preparation.

5.13. Distribute a copy of the EPA instructions and reporting sheet with the samples.

5.14. Establish a due date for the analysis, allowing sufficient time to record and mail the data to EPA to meet their stated deadline.

5.15. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.16. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

7.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

7.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. Liquid waste.

8.1.1. Dispose of radioactively contaminated liquid waste in a sink specifically approved for the disposal of aqueous radioactive waste and inorganic acids and bases.

8.2. Solid waste.

8.2.1. Accumulate radioactively contaminated solid waste (such as paper wipes, glass or plastic pipettes, plastic cups, and incorrectly spiked QC samples) in a covered metal can lined with a plastic bag and keep it segregated from nonradioactive solid waste.

8.2.2. Label the can to indicate its use for radioactively contaminated waste.

8.2.3. Open the can only for the time necessary to add waste.

8.2.4. When the plastic bag is full, seal it with tape, remove it from the can, and identify it as radioactively contaminated waste.

8.2.5. Put a new plastic bag into the waste can for continued use.

8.2.6. Place the sealed bag into a cardboard box lined with a plastic bag and labeled to indicate its use for radioactively contaminated waste.

8.2.7. When the cardboard box is full, seal the plastic bag liner and the box.

8.2.8. Mark the box as radioactively contaminated compactable waste and, on the outside of the box, reference the current Waste Profile Form (WPF) describing the waste in the box.

8.2.9. Line a new box with a plastic bag and label it for continued use.

8.2.10. Complete the current Radioactive Solid Waste Disposal (RSWD) Record describing the full, sealed box of waste. Reference the current WPF number on the RSWD.

8.2.11. The outside of the full box is surveyed for radioactive contamination by a radiation control technician. Record the results of the survey on the RSWD.

8.2.12. Submit the completed RSWD and a copy of the WPF to Waste Management (CST-7) for approval.

8.3. Waste pickup.

8.3.1. After the RSWD describing the full box of solid waste has been approved by CST-7, request pickup of the box by the contractor approved for the transportation of radioactive contaminated waste. A written job order may be required to request pickup of the waste.

8.3.2. The RSWD and a copy of the associated WPF accompany the full box.

8.3.3. The waste is disposed of according to Laboratory policy.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

9.6. "Low-Level Radioactive Solid Waste," Administrative Requirement 10-2, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

9.7. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

EPA TRITIUM IN WATER PERFORMANCE EVALUATION STUDY

Analyte: Tritium	**Method No.:** QCS230
Matrix: Water	
Procedure: Liquid scintillation counting	
Effective Date: 01/01/85	**Authors:** Carolyn J. Macdonell Nancy L. Koski Margaret A. Gautier

SAFETY NOTE: Before beginning this procedure, read all of the material safety data sheets for the chemicals listed in Sec. 4. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 8 of this procedure for proper waste disposal practices.

1. Principle of Method

1.1. The United States Environmental Protection Agency (EPA) submits water performance evaluation samples for tritium analysis.

2. Collection and Storage of Samples

2.1. No dilution or aliquoting is required.

2.2. Samples are stored at room temperature pending analysis.

3. Apparatus

3.1. Chain-of-custody tape.

3.2. Labels printed with quality control (QC) sample numbers.

4. Reagents

4.1. None required.

5. Procedure

5.1. The tritium sample is received in a small bottle. A blank is received in a second bottle.

5.2. Seal the bottles with chain-of-custody tape.

5.3. Label the bottles with QC sample numbers. The same QC sample number may be used for replicate aliquots taken from the bottle by the analyst.

5.4. Store the samples at room temperature pending analysis.

5.5. Submit one QC sample (NEVER A BLANK) prepared as described in Method No. QCR270, Tritium in Water—QC Sample Preparation.

5.6. Distribute a copy of the EPA reporting sheet with the samples.

5.7. Establish a due date for the study, allowing sufficient time to record and mail the data to EPA to meet their stated deadline.

5.8. Record the performance evaluation study identity, agency, sample numbers, sample descriptions, date received, date due, dilution and aliquoting information, matrix, and analysis requested in the QC Laboratory notebook, the External Quality Assurance Samples notebook, and the CVD database on the VAX.

5.9. Deliver the samples and all paperwork to the Sample Management section for distribution to the analysts.

6. Reporting of Results

6.1. When the analyses are completed, fill out the EPA report sheet. Make sure that the units of the reported results match those requested on the EPA report sheet.

6.2. Send the completed report form to EPA by the required EPA deadline.

6.3. Record the results and the date the report was sent to EPA in the External Quality Assurance Samples notebook on the appropriate sheet.

7. Performance Evaluation Certified Values

7.1. When the certified values for the performance evaluation samples are received from EPA, enter the values on the appropriate sheet in the External Quality Assurance Samples notebook.

8.2. Record the sample number, certified value name, certified results and uncertainties, certified value units, code, and N reference in the CVS database on the VAX.

8.3. File the completed report in the Quality Assurance and Data Management section files and send a copy of the report to the section in which the analyses were performed.

8. Proper Waste Disposal Practices

8.1. No radioactively contaminated waste or hazardous waste is generated using this procedure.

9. Source Materials

9.1. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1987," Los Alamos National Laboratory report LA-11454-MS (1988).

9.2. M. A. Gautier, E. S. Gladney, M. B. Phillips, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1988," Los Alamos National Laboratory report LA-11637-MS (1989).

9.3. M. A. Gautier, E. S. Gladney, N. L. Koski, M. B. Phillips, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1989," Los Alamos National Laboratory report LA-11995-MS (1990).

9.4. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, and B. T. O'Malley, "Quality Assurance for Health and Environmental Chemistry: 1990," Los Alamos National Laboratory report LA-12208-MS (1991).

9.5. M. A. Gautier, E. S. Gladney, N. L. Koski, E. A. Jones, B. T. O'Malley, G. H. Brooks, and W. D. Moss, "Quality Assurance for Environmental Chemistry: 1991," Los Alamos National Laboratory report LA-12436-MS (1992).

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