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Measurement Trends for Future Safeguards Systems

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ABSTRACT

Safeguards for future commercial-scale nuclear facilities may employ three materials control and accounting concepts: classical accounting, dynamic materials balancing, and independent verification of inventories and materials balances. Typical measurement needs associated with the implementation of these concepts at high-throughput facilities are discussed. Promising measurement methods for meeting these needs are described and recent experience is cited. General directions and considerations for meeting advanced safeguards systems needs through measurement technology development over the next decade are presented.

I. INTRODUCTION

Safeguarding the high-throughput nuclear facilities anticipated to operate in the 1990's engenders scientific and engineering challenges for measurement technology development for the next decade. In conjunction with the planning and design of these facilities, systems studies are being conducted in the US and other nations to establish future safeguards performance capabilities and identify deficiencies in existing technology. As a result, measurement technology needs for advanced domestic and international safeguards systems are beginning to emerge.

Materials control and accounting at future facilities may include classical materials balancing, dynamic materials accounting, and the verification of inventory and materials balance data by an independent inspection authority. The differing objectives of each activity often impose special requirements on needed measurement technology. The classical closure of a materials balance places the premium on accurate and precise techniques, while dynamic materials accounting favors criteria associated with timeliness. The verification of inventories and materials balances requires inspector measurement capability that is independent of plant operator results.

Measurement needs encompass more than the availability of techniques for prescribed nuclear material characteristics. Concomitant measurement control programs and operational features are essential complements for truly meeting the needs of the safeguards system. It is precisely in the complementary features associated with the use of a measurement technique that the distinctions among the three materials control and accounting concepts become most evident.

In this paper, the topical measurement needs suggested by existing systems studies and experience are reviewed and selected measurement problems referenced. These selected measurement needs typify the spectrum of measurement problems that must be addressed during the next decade to achieve the performance demanded of future safeguards systems. Clearly, many additional measurement needs will emerge in detail as facility-specific plans for implementing advanced safeguards concepts are generated.

Promising measurement methods for meeting these needs and recent experience documented in the current literature are cited. Specific areas of technological deficiency are identified for research and development emphasis in the future. Throughout the overview of measurement methods, the role of the measurement is continually related to the appropriate materials control and accounting concept. Special attention is devoted to relatively simple measurement techniques formerly disregarded as being too imprecise or inaccurate for "accountability measurements."

The concluding section considers directions for future measurement technology development in the light of advanced concept demonstrations that are the necessary prelude to full-scale implementation in the nuclear facilities of tomorrow.

II. TOPICAL MEASUREMENT NEEDS FOR FUTURE SAFEGUARDS SYSTEMS

Available systems studies of commercial-scale facilities and documented experience from existing facilities have contributed to the understanding of advanced safeguards system measurement needs. On the basis of these results, the topical areas encompassing prominent measurement needs for each concept are discussed below.

A. Classical Materials Balance Accounting

The classical concept of materials accounting is based on the definition of a materials balance area (MBA) encompassing all or a portion of a nuclear facility, the measurement of all nuclear material transferred across the boundaries, and the determination of the physical inventory within the MBA at discrete times.

Severe limitations in timeliness and sensitivity are inherent in the concept of classical materials balancing. The quality with which the classical balance can be closed, however, is intimately related to the efficacy of dynamic balancing and safeguards inspection concepts for high-throughput facilities. Planning and development to resolve the needs of the classical concept consequently enhance the potential detection capabilities sought from the companion concepts.

1. Bulk Measurements. The need for improvements in bulk measurement concepts, systems, and instrumentation for irradiated nuclear fuel reprocessing and conversion facilities is almost universally recognized.^{1,2,12} One systematic evaluation of the error components³ shows that the bulk input measurement alone contributes 42% of the total inventory difference error, roughly as much as the aggregated contribution of the uranium feed, product, and waste measurements! Other experience⁴ indicates that the calibration and stability of calibration during operation can result in a relative error of 1% or more and that "the bulk volume measurement is the weakest point in the overall SNM accountancy of relevant facilities." The effects of bulk measurement errors on the quality of materials balance accounting can invalidate the utility of enhanced or improved assay capability.

2. Measurement Control. Regardless of analytical precision improvements, the sensitivity of materials accounting is limited by the efficacy of physical standards and calibration procedures and the validity of the error characterization for process materials measurement.^{1,5-7} Measurement errors, including those with temporal or operator dependence, can be identified, estimated, and addressed only through rigorous and comprehensive measurement control programs.

New measurements envisioned for high-throughput facilities will require the development of physical standards and methods for establishing, monitoring, and maintaining measurement control. The magnitude of this effort will vary according to the measurement technique, the specific application, and the desired technical performance of the measurement in the materials control and accounting system.

3. Scale-Related Problems. The expanded scale of high-throughput facilities presents special problems not observed in existing facilities. In a commercial-scale facility, for example, waste streams and processing residues may contain significant quantities of nuclear material requiring quantitative analysis and assay instead of relatively simpler threshold measurements. Dissolver sludge and the content of leached hulls from reprocessing are examples of accountability problems arising predominantly from the magnitude of the throughput.^{1,8} For example, between 0.01 and 0.11% of the plutonium in irradiated PWR fuels can remain undissolved after treatment with 3-4 M HNO₃.⁹ These low concentrations cannot be used to conceal short-term diversion but could be used to mask protracted diversion.¹⁰

The high-throughput of future facilities will require corresponding assay-rate capabilities of measurement systems. Although certain measurement methods are currently capable of meeting the technical performance requirements, the operational features preclude their consideration for high-throughput applications. Automated features must be explored and developed during the next decade to ensure that adequate analytical methods, including sampling and preparation, are economically feasible and warranted by cost-benefit analysis.

Even under ideal operating conditions, high-throughput facilities will generate significant quantities of scrap and recycle materials for which representative sampling is not possible or practical. Certain high-throughput facilities could produce 20-30% or more off-specification recycle material¹¹ depending on feed characteristics and user quality control requirements. The importance of scrap recycle, particularly from intermediate processing stages, is that substantial quantities appearing in the materials balance may not be amenable to feed- or product-quality measurements.

B. Dynamic Materials Accounting

To complement classical accounting at future commercial-scale facilities, dynamic materials balance concepts have been designed to bridge the void in accounting information between physical inventories. Dynamic materials accounting is currently being implemented in numerous US facilities and has been proposed and investigated as a method for meeting the timeliness and sensitivity goals of the International Atomic Energy Agency in future high-throughput facilities.^{12,13}

Dynamic materials accounting features estimating, deriving, or measuring the in-process inventory, the analog of the ending physical inventory in the classical accounting concept, during process operation. In addition, dynamic

materials accounting concepts incorporate rapid measurement systems that provide materials balance data in times that are short compared to the interval between physical inventories.

1. Flow Measurements. Traditionally, flow measurement technology was developed primarily for process control. Over the last few years, however, flow measurement needs for dynamic safeguards applications have been recognized and received more attention. Although sometimes used in classical accounting, e.g., waste discharge monitoring, stream flow measurements are essential for establishing the interim in-process inventory in high-throughput reprocessing facilities and may be necessary for smaller-scale operations.

Flow measurement systems for reprocessing plants are subject to radiation fields, corrosive environments, and sometimes virtually inaccessible locations. Accuracies in the range of 0.5-1.0% have been demonstrated for various systems under laboratory conditions.^{1,8} Although such technical performance appears to be sufficient for most dynamic safeguards applications, suitable operational features and protracted in-situ experience have not been documented.

2. Rapid Intermediate Analytical Capability. To provide substantial improvements in the timeliness of the dynamic accounting, new measurements of intermediate processing materials must be available in times significantly shorter than required for physical inventories. This typically includes measurements previously performed for process control and not for classical accounting. Such measurements need not be limited to in-line NDA; rapid sampling, transfer, and analysis capability is also useful. These measurements are necessary to subdivide classical MBAs to improve diversion detection sensitivity and localize diversion. In reprocessing facilities, such measurements have been proposed to separate the codecontamination-partition and the partition-plutonium purification cycles. For conversion facilities, measurements could be added to separate the continuous liquid process from the batch-operated solids handling area. The LASL safeguards system conceptual design series (including Refs. 1 and 8) provides a description of these new measurement requirements for a variety of nuclear facilities.

3. Use of Process Control Information. Much information on process variables such as flow rates, tank volumes, temperature, acidity, and density presently is required to establish and maintain equilibrium during process operation. Much of this information when supplemented with laboratory analytical measurements can be used directly or with some instrument improvements for dynamic materials accounting.¹ Conversely, safeguards information can be used for process control to establish and monitor the continuity of equilibrium operation.

C. Materials Balance and Inventory Verification

The third area of importance for the development of measurement technology is the independent verification of the results of materials control and accounting by inspection organizations. Both international and domestic safeguards employ independent measurement verification to establish the quality and validity of facility operator measurements individually and collectively. Verification of the quantity and location of nuclear material is patently the basis of international safeguards. Although independent verification is

perhaps not the sine qua non of domestic safeguards, the role of independent measurements in future domestic inspection activities is anticipated to expand over the next decade.

Measurement needs for the independent inspection of high-throughput facilities are intimately related to the presently evolving details of the facility-specific approach chosen by the inspection authority. The general areas discussed below, however, may be anticipated regardless of the detailed plans for future implementation.

1. Special Measurements Requirements. Some measurements currently of little interest for domestic safeguards may be required by future independent and international inspection concepts. The verification of enrichment plant feed, for example, derives importance for independent inspection. Special measurement requirements may take the form of new key measurement points or be related uniquely to independent inspection activities such as reestablishing inventories after loss of containment and surveillance. Spent-fuel measurements are of particular interest for verifying receipts at reprocessing facilities or away-from-reactor sites, and has been considered as an additional key measurement at reprocessing facilities.¹⁴⁻¹⁶

2. Adaptations of In-Plant Instrumentation. It is intuitively clear that some reliance on in-plant instrumentation capable of high precision and accuracy must be included in the inspection strategies for commercial-scale facilities to achieve detection capabilities better than 1% of throughput. Preliminary steps have been taken in the US,¹⁷ and the matter has been considered by the IAEA for some time.¹⁸ Tamper resistance and the capability for establishing and verifying the calibration are primary considerations that must be addressed over the next decade.

3. Improved Portable and Transportable Inspection Measurement Capability. Some analytical and nondestructive methods designed for high precision and accuracy must be simplified and modified for meeting the in-the-field needs of inspectors. Particularly striking analogs of more sophisticated technology include the active well coincidence counter,^{19,20} the ion chambers for spent-fuel examination,²¹ and the quadrupole mass spectrometer.^{22,23} Portable and transportable instrumentation for bulk measurements represent an essential complement to analytical techniques for verifying plant operator statements of inventory and materials balance. Certainly characterization of the measurements, again through rigorous and long-term measurement control programs, must be undertaken for the same reasons as in the classical case.

III. SELECTED TRENDS IN FUTURE SAFEGUARDS MEASUREMENT TECHNOLOGY

Quantitative safeguards measurements generally feature the investigation of one or more of the bulk, nuclear, or atomic properties of the nuclear material. Bulk methods examine macroscopic or mesoscopic physical variables such as mass, volume, or temperature. Isotopic and elemental methods are based on the unique nuclear and atomic characteristics of the material of interest and are frequently a necessary complement to bulk methods in materials accounting concepts. It is not the purpose of this paper to provide a comprehensive review of recent developments in measurement methods for nuclear materials. Rather, we wish to highlight trends and directions in measurement technology development likely to meet the technical and operational performance needs of future safeguards systems.

A. Bulk Measurements

Volume, density, and mass measurements are fundamental to the application of classical accounting, and decades of operational experience in a variety of nuclear facilities are available. Recent developments and operational experience over the next decade are expected to engender dramatic improvements that are particularly germane for commercial-scale reprocessing and conversion facilities.

1. Volume. One of the most technically challenging problems in this area is the bulk measurement of irradiated nuclear material during reprocessing. NBS has recently developed a transportable high-precision system for remote tank calibration and verification.²⁴ Prototype laboratory experience has demonstrated 0.02% short-term uncertainty in water volume transfers. Promising current experience with high-precision electromanometers at SRP, ICPP, AGNS, and Tokai-mura suggest calibration errors in volume and density measurements can be reduced to one or two tenths of 1% or less.^{3,24,25} An NBS study of in-tank solution-density measurements has demonstrated that, with careful temperature monitoring during measurements, an accuracy of 2.2 parts in 10^4 is achievable, comparable to laboratory precision with a mitigation of systematic sampling effects.²⁵ Experiments conducted to date at the above facilities have employed water or cold nitrate solutions. There is considerable debate on the precision and accuracy, e.g., calibration stability, potentially achievable by these methods under prolonged operational reprocessing conditions. Long-term operational experience and evaluations are needed.

2. Density. Density measurements have been used traditionally in reprocessing plants to estimate fissile concentrations in process tanks for process and criticality control. This approach has been investigated in a recent study¹ as a means of determining the in-process inventory for dynamic materials balancing in both a 200 MTHM/yr (metric tonnes of heavy metal per year) and a commercial-scale 1500 MTHM/yr reprocessing facility. For safeguards purposes, the nonspecificity of density/acidity methods requires complementary information from nuclear or atomic methods to convert bulk property measurements into fissile concentrations. The main advantages of this approach for dynamic materials balancing are that measurements are available virtually instantaneously and that density/acidity instrumentation is normally installed for process control. Formal closure of dynamic materials balances is accomplished by updating or verifying the uranium or plutonium estimates using results of chemical or nondestructive analyses as they become available.

Density methods for estimating fissile concentrations are sensitive to variations in the HNO_3 concentration and temperature.^{26,28} In addition, fissile estimates by density methods suffer some loss in precision for concentrations less than 50 g/l. Future research and development are required to demonstrate the full potential and limitations of such methods and their utility in a safeguards systems context.

As stated at the outset of this section, the accurate and precise assay of the input accountability vessel in a reprocessing facility presents a formidable challenge to plant operators. Verification of the contents by an independent inspection authority is even more difficult. High-precision density/acidity methods have been considered recently as a means of verifying uranium, plutonium, and thorium concentrations in both head-end and product streams.^{1,26,28}

In an interesting application²⁶ based on high-precision, controlled-temperature, capillary-resonance density measurements and shipper's burnup estimates, relative standard deviations of 0.8-1.2% were reported for determining the uranium concentration of LWR dissolver solutions. Product nitrate results of 0.2% and 1.2-2% on the uranium and plutonium concentrations, respectively, were also obtained. Variations in the plutonium valency and the relatively larger variations in the HNO₃ concentrations have been suggested as possible contributors to the larger plutonium product errors.

3. Flow. Because the closure of a classical materials balance is essentially a static process, stream flow measurement methods and instrumentation have received limited safeguards attention. Flow measurement capability is critical, however, for the dynamic closure of materials balances in near-real time.^{1,11} The results of these studies assume the availability of instrumentation with precisions of 5% and calibration errors of 1% to estimate the in-process plutonium inventory of contactors and groups of contactors to 5-10% during actual operation.

Two possible methods for exceeding these flowmeter performance requirements are the heat-pulse and Coriolis-force flow methods. ORNL is currently investigating a concept based on the application of a heat pulse to a pipe followed by a measurement of the transit time to a heat-sensitive detector downstream. Preliminary results indicate that a precision and accuracy of 1% or better can be achieved. Coriolis-force flowmeters have been studied by AGNS²⁹ and ORNL for reprocessing product stream applications. Additional investigation is required to verify manufacturer's claims of 0.5-1% precision under routine operating conditions. Unlike the heat-pulse method, piping modification is required. Both methods require an evaluation of operational features such as repair, replacement, and transient environmental conditions for a practical utility assessment in future high-throughput facilities.

Investigators at NBS have recently examined the relative merits of various flow measurement methods for use in reprocessing plant canyons. According to these studies,²⁷ the most promising method is based on a nonwetted capacitive-probe noise-correlation principle. This flow measurement concept features no interruption of the process flow and requires putting only small metal capacitor plates around a nonconducting section of the process line. This sensor can be completely contained within a stainless-steel shell welded to the process line. The associated electronic instrumentation can be located outside the canyon environment in an area normally accessible to plant operators.

To evaluate the relative technical performance of flow measurement systems used in nuclear facilities, NBS has developed a laser Doppler velocimeter as a reference measurement method. This system provides a unique capability for measuring spatial velocity correlations and is anticipated to provide definitive performance characterizations of safeguards flow measurement technology.

B. Isotopic Methods

Isotopic methods rely on the signatures generated by induced or spontaneous nuclear transformations or by the characteristic motion of nuclei in electromagnetic fields. On the microscopic level, nuclear reactions give rise to neutrons, gamma-rays, and alpha and beta particles with presumably well-known probabilities. In finite samples, the primary reaction products can initiate subsequent reactions and even sequences of reactions. The fundamental problem of isotopic measurement methods is quantifying the relation of the

emissions from a finite sample to its fissile and fertile components. In actual practice, the problem is often compounded by the presence of "matrix" materials and geometric effects. In general, there are two approaches to solving the ubiquitous matrix problem: using theoretically determined matrix corrections, or corrections determined empirically through the fabrication and measurement of sufficiently representative calibration standards. These approaches are presently being employed in solving today's measurement problems. More expansive efforts in this area will be required to address measurement needs that are not present as pilot-scale facilities.

1. Neutron methods. Neutron techniques are anticipated to play a significant role in the classical and dynamic materials accounting concepts for future high-throughput facilities, particularly for the measurement of recycle, intermediate product, and irradiated feed and waste materials. Passive neutron techniques in common safeguards applications generally require a correction for (α, n) neutrons resulting from alpha decay by the plutonium isotopes and subsequent interactions with light matrix elements. Spontaneous fissions of the even plutonium isotopes liberate 2 or 3 neutrons per fission, and coincidence counting is conventionally employed to resolve time-correlated spontaneous fission and random background events. Considerable effort over the years has been directed toward coincidence counting, including the development of new electronic circuitry. For plutonium samples of more than a few grams, passive neutron assays based on coincidence counting involve corrections for multiplication effects. The advent of fast electronic circuitry and theoretical investigations now make it possible to correct coincidence counts for multiplication effects in large quantities of oxides (including the presence of H_2O), metals, and other well-characterized materials.³⁰ Recent comparisons of circuitry seem to indicate the marked superiority of shift register coincidence systems.^{31,32}

A recently explored alternative approach to coincidence counting is based on the analysis of the neutron count distribution.³³⁻³⁵ In this approach, the assay of plutonium is derived from the observed departure of the neutron count distribution from the Poisson background distribution. One investigation based on theoretical calculations shows the distribution method to be superior to twin-gate coincidence counting for high pulse rates.³³ Further studies have extended the theoretical formalism to include detector dead time, neutron multiplicity, and multiplication in addition to contributions from (α, n) interactions. Experimental results to date indicate that the distribution method may be competitive with coincidence counting and offer some advantages.^{34,35} No definitive comparison of the neutron count-distribution method with shift-register coincidence counting is yet available.

On the basis of trends visible today, active neutron techniques are likely to be used in future commercial-scale facilities for the measurement of irradiated materials such as dissolution residues and hulls and plutonium oxalates, salts, filtrates, and other residues. These measurement problems are typically characterized by high density, radiation, and (α, n) fields that prohibit the use of simpler methods.

Experience with in-plant active neutron-interrogation instrumentation is currently being accumulated. Selected systems and performance as cited by the instrumentation developers or users are shown in Table I. Active neutron-interrogation methods for solid, fission-product-contaminated LWR reprocessing waste must deal with high spontaneous-fission-neutron backgrounds from the curium isotopes. Data from La Hague indicate that delayed neutron counting

TABLE I

Selected Neutron Measurement Results from In-Plant Systems

<u>Material Composition</u>	<u>Method Description</u>	<u>Performance</u>	<u>Comments</u>	<u>Ref.</u>
HEU Irradiated dissolution residues	Cyclic Cf-252 neutron irradiation/delayed neutron counting	~1% precision projected	Results based on Monte Carlo calculations of design	36,37
Irradiated LWR and FBR hulls - Pu	Cyclic 14-Mev neutron irradiation/delayed neutron counting	Accuracy ~20% for 1% residual fuel	Results for unaged fuels compare favorably with gamma-ray methods	38
Pu fluorides, slag and crucible	Passive and (active minus passive) Random Driver	2-5% precision less than 5% accuracy	The difference in active minus passive results is independent of (α, n)	39
HEU oxides, metal, and processing residue	Random Driver or Active Well Coincidence Counter	0.5-5% precision	AWCC more stable, but more sensitive to inhomogeneities	20
HEU fabrication scrap	Cyclic Cf-252 neutron irradiation/delayed neutron counting (Shuffler)	0.1-0.4% precision on standards. ~1% on individual scrap categories	In-plant data under study to delineate material categories for individual calibrations	11
Pu oxalate from FFTF fuel fabrication	Ratio of double-ring singles and coincident neutrons	2-4% accuracy	Limited data available	40

following cyclic irradiation from a 14-Mev accelerator yields results comparable to gamma-ray methods for irradiated LWR and FBR hulls. Presumably, the neutron method is relatively insensitive to the age of the fuel, unlike the gamma-ray methods. A photoneutron method has been proposed by European investigators and uses active-passive interrogation to resolve the fissile components. An alternative method is based on cyclic irradiation from a Cf-252 source and delayed neutron counting. The latter two methods have reached the commercial-scale conceptual design stage, but no in-plant experience is available.

Another significant problem, the measurement of plutonium processing intermediates and residues, has been investigated by a variety of active neutron approaches. An apparently promising technique for salts and residues is based on a variation of the Random Driver. It has been shown that separate active and passive assays of certain processing residues with an adaptation of the Random Driver can be combined in a manner insensitive to multiplicative effects arising from (α, n) reactions. Because two independent measurements are involved, statistical precision is degraded, but no other NDA technique has been shown to produce consistently comparable results.

The in-situ application of advanced neutron methods frequently requires a detailed investigation of isotopic and matrix variations associated with normal processing operations. An exemplary study is currently underway in connection with the in-plant evaluation of the Cf-252 Shuffler at Savannah River Plant.¹¹ Although the instrument was designed for the measurement of the U-235 content, assay results are somewhat sensitive to the even-isotope composition of the samples. Important concomitant efforts have addressed the variations in the isotopic compositions encountered during normal processing and the consequent effects on the validity and accuracy of calibration. Such investigations play a vital role in characterizing the (sometimes unrecognized) errors associated with in-plant measurement applications.

Plutonium oxides, oxalates, and other intermediate processing materials often pose special measurement problems caused by the presence of substantial quantities of moderating compounds, especially H₂O. One approach to the measurement of plutonium oxalate formed in the process of FFTF fuel fabrication is based on a double-ring, thermal-neutron coincidence counter.⁴⁰ The principle involves the measurement of the coincidence-to-gross-neutron ratio at two separate radii from the sample chamber. Available data are limited, but encouraging; it is not clear how far the method can be extended. Alternatives for measuring H₂O content are radio frequency and x-ray or neutron scattering to supplement theoretically determined corrections to shift-register coincidence counting. No definitive measurement technique has been established for this important class of nuclear materials.

Although specific applications often pose special problems, the theories of active and passive neutron measurement methods are reasonably well-known; qualitatively different methods are not likely to emerge over the next decade. The active techniques will require substantial effort to provide demonstrated technology for the special problems associated with future high-throughput facilities. Active neutron instrumentation tends to be rather sophisticated and sensitive to variations in the type of material to be measured. As a result, calibration procedures, calibration stability, physical standards, and variability in processing environments must be addressed emphatically over the next decade. Reference measurement methods such as resonance neutron radiography⁴¹ are being developed to validate calibration and calibration stability for in-plant neutron instrumentation. Projects and programs,^{10,42-44}

including long-term measurement control studies, have been initiated for some nondestructive assay applications and are essential for obtaining reliable measurements having well-characterized errors.

2. Alpha spectrometry. In-line alpha monitors are used in reprocessing plants to measure plutonium concentration in waste and recycle streams. The instruments were developed for process control but are applicable for safeguards measurements and are required to partition effectively a reprocessing plant into additional unit process accounting areas for dynamic accounting. Instruments tested at AGNS can measure plutonium in aqueous and organic streams with a precision of 12%.⁴⁵ A French-developed rotating-drum monitor routinely measures plutonium with a precision of 3% for aqueous and 4.5% for organic streams.⁴⁶

C. Elemental Methods

Elemental methods are based ultimately on properties of atoms or molecules or transitions in the atomic- or molecular-electron shells. Methods based on atomic orbital transitions include x-ray fluorescence, absorption-edge densitometry, and electrochemistry. Photometric and spectrophotometric techniques used in safeguards applications generally rely on the specific nature of molecular-electron energy-level transitions. Many elemental methods offer advantages over classical techniques, primarily because they yield relatively direct, rapid information about the atomic species present. As a result, fewer complementary measurements are required to compute the quantities of safeguards interest. Usually, elemental methods require minimal sample manipulation thus facilitating error characterization as well as providing operational benefits. These attractive features portend a key role for elemental methods in future advanced safeguards systems.

1. X-ray fluorescence. X-ray fluorescence has been applied over the years to a wide variety of samples and is a candidate for future on-line measurements of reprocessing solutions. Selected x-ray fluorescence methods developed or proposed for reprocessing applications are summarized in Table II. Recent studies suggest that x-ray fluorescence with high-resolution crystals, electronic signal filtering, and computer-generated corrections might be competitive with conventional mass-spectrometric methods for the analysis of dissolver solutions. Current efforts in the development and application of theoretical methods and algorithms for interference and matrix corrections to K x-ray spectra⁵⁵ may provide progress toward the solution of the inherent x-ray attenuation, self-absorption, and incoherent scattering problems in this x-ray region. The method may be somewhat sensitive to calibration quality and matrix effects caused by normal processing variations. The magnitude of these effects is the subject of a forthcoming in-plant evaluation.

X-ray fluorescence is the basis of a total sampling concept designed to address the current practical assay problems associated with inhomogeneities, precipitates, polymers, and perhaps batch-to-batch heel effects in the front-end accountability vessel.⁵⁶ Although numerous technical and operational features remain to be demonstrated, the potential benefits of the concept warrant further investigation.

TABLE II

Applications of X-Ray Fluorescence to Reprocessing Samples

<u>Type of Sample</u>	<u>Conc. Range, g/L</u>	<u>Radiation Levels</u>	<u>Comments</u>	<u>Ref.</u>
FBR fuels; after partition	Pu:1-20	1 Ci/L	WD; yttrium IS	47
LWR; dissolver solution	Pu:1-3	1000 Ci/L	WD evaporate on filter paper	48-50
LWR fuels	U:20-40 Pu:0.2-0.4	1000 Ci/L	WD	51
Product Solution	Pu,U:0.001-4	100 Ci/L	ED selenium IS	52
Dissolver Solution	U:50 Pu:0.15	1000 Ci/L	ED	53
LWR Dissolver Solution	U:300 Pu:3	1000 Ci/L	ED; development stage	54

IS = internal standard

WD = wavelength-dispersive spectrometer

ED = energy-dispersive spectrometer

2. X-ray absorption-edge densitometry. Absorption-edge densitometry offers distinct technical and operational advantages over conventional analytical techniques for certain nuclear fuel cycle applications. The method is based on the measurement of the transmission ratio just above and below the x-ray absorption edge of the element of interest. Selectivity is limited only by the ability of the spectrometer to resolve spectral contributions from irrelevant elements with neighboring absorption edges. An inherent technical advantage of the method is the relative insensitivity to matrix effects, i.e., the measured transmission ratio becomes independent of matrix contributions as the two transmission measurements approach the absorption edge of the element of interest.

X-ray densitometry has been developed in this country for rapid in-line determinations of nuclear materials such as uranium or plutonium in concentrated product streams.⁵⁷⁻⁶² More recently interest in the method has been expanded to determination of uranium and plutonium in streams that contain fission products, and the technique is being investigated for the determination of uranium in dissolver solutions. Plutonium cannot be determined in dissolver solutions for light-water reactor fuels because of the high uranium-to-plutonium ratio; however, the method may be applicable to determination of both uranium and plutonium in fast-breeder-reactor dissolver solutions where the uranium-to-plutonium ratio is approximately 5:1.

Extended in-plant operational experience at an HEU recovery facility has shown that absorption-edge densitometry is competitive with colorimetric chemical analysis, in terms of technical performance, and is markedly superior on the basis of timeliness and operational costs.⁴² In addition, the long-term measurement control and comparison program to document these results facilitated the identification and characterization of previously unsuspected errors.⁴² A similar evaluation of densitometry applications for plutonium solutions is underway at Tokai-mura, Japan,⁶³ and is planned for the Savannah River Plant.

Absorption-edge densitometry measurements are key elements in the dynamic materials balance concepts proposed for commercial-scale reprocessing and conversion facilities.^{1,11} Critical concentration measurements of the LBP and 3PCP streams by absorption-edge densitometry allow the front end and plutonium purification areas to be treated as distinct unit process accounting areas. Laboratory and off-line experience has demonstrated the requisite technical performance characteristics demanded by these concepts. However, demonstration of in-line measurement performance under operational conditions for a commercial-scale facility is required.

3. Spectrophotometry. Spectrophotometric methods for safeguards accounting measurements traditionally have been discarded on the basis of technical performance. The inherent operational features of timeliness and economy, however, may offer potential solutions to certain future assay rate requirements, particularly when companion analytical chemistry steps can be automated.

The in-line spectrophotometric determination of uranium has been used in reprocessing plants as a process control method for determining uranium in the uranium product streams for a number of years.^{64,65} The precision of the method has been in the range of 5-10%, which has been adequate for process control. Recent investigations at ORNL are aimed at improving the precision and accuracy of the method for safeguards determination of uranium.⁶⁶ Precisions of ~5% have been documented; however, using improved techniques it is conceivable that the precision of the method can be improved to the range of 1-2%. The method also is being investigated for the determination of tetravalent plutonium in process streams. Using quartz fiber optics the method can be applied in-line to reprocessing-type solutions that have significant beta-gamma radiation fields.

Spectrophotometric methods need not be applied in-line to be attractive for dynamic materials balancing. If measurements can be obtained rapidly off-line with minimal chemical manipulations, the methods may be competitive with NDA methods and in some cases may provide better precision and accuracy. For example, the French have developed a rapid off-line technique for determination of plutonium in reprocessing samples and have even applied the method to dissolver solutions.⁶⁷ In this method an aliquot of the sample is drawn from the line, plutonium is oxidized to the hexavalent state with silver peroxide, and the absorptivity of the hexavalent plutonium band at 816 nm is measured. To improve the precision and accuracy of the method, neodymium may be added as an internal standard. Using the internal-standard technique, accuracy of better than 1% with a precision of 1.5% has been claimed.

4. Fluorometry. Fluorometry has been used for years in a variety of applications ranging from trace uranium determination in biological samples to uranium ore prospecting. Conventional fluorometry requires sample drying and fusion, and sintering into pellets, sometimes preceded by separation of the uranium from many of the matrix elements. Recently a pulsed-laser fluorometric method for direct uranium measurements in solution has been developed at New Brunswick Laboratory.⁶⁸ In addition to the obvious operational advantages, a comparative evaluation with the conventional method demonstrated a lower sensitivity of the pulsed-laser method to matrix effects. Precision and accuracy of 2-3% is claimed with an analysis time of a few minutes, in contrast to a precision of 10-12% for the conventional method with careful control of operating procedures.

5. Electrochemical methods. Electrochemical methods including potentiometry, coulometry, amperometry, and polarography, have been well developed over the years for determination of both uranium and plutonium in a wide variety of nuclear materials. The methods generally have been developed on a laboratory scale and require careful chemical manipulations to attain the required precision of better than 0.5%. The methods also have drawn interest for rapid off-line determinations of plutonium and uranium in process-type samples.

In-line polarography has been considered as a process control measurement for uranium in waste streams.⁶⁹⁻⁷² Although significant development work was performed the method was never implemented.

Off-line coulometry is being considered for rapid high-precision determination of both uranium and plutonium in product streams. Precision of 0.1-0.2% is obtained for 5-mg plutonium samples using an automated coulometer.^{73,74} Although the sample must be removed to the analytical laboratory, analysis time per sample is 0.5 min.

IV. DIRECTIONS FOR FUTURE MEASUREMENT TECHNOLOGY DEVELOPMENT

The traditional phase of safeguards measurement technology development is nearing its completion. In the past, research and development activities were directed toward "single point - single component" measurement problems in the nuclear fuel cycle. The historical concern has been two-fold: what methods appear promising and what is the best technical performance that can be achieved? In this light, remarkable progress has occurred over the last decade.

During the next decade, this necessary but parochial approach must be broadened to encompass the composite performance of the individual measurement components and the needs of the relevant materials accounting concept. Equitable comparisons of alternative combinations of measurement methods will be required to evaluate performance in the systems context. It is, after all, the system that is generally designed to detect diversion, not the component measurements per se.

In view of the new emerging interim accounting concepts for domestic and international safeguards, future research and development must also investigate optimization features other than precision and accuracy. The simple measurement principle that seemingly has no place in classical accounting may be ideal for estimates of in-process inventory, process and safety control, or in-the-field inspection applications. In addition to explorations at the frontier of accuracy and precision, "counter-trend" developments may fulfill important technological needs with the benefit of enhanced or superior operational

features. Examples in evidence today include alpha monitoring, spectrophotometry, quadrupole mass spectrometry, active well coincidence counting, and the pulsed D-T interrogation system discussed at this conference.⁷⁵ Each of these developments derives its importance from the specific needs of today's, and perhaps tomorrow's, safeguards systems.

The scale of future commercial facilities in itself engenders a new and challenging breed of measurement problems that is often absent in pilot-scale versions. Systems studies as well as intuitive concerns have pointed out the need for internal measurements for in-process inventory estimates, transfers between adjacent unit processes, and new key measurement points. In addition, certain waste streams containing de minimis quantities in pilot-scale facilities become significant in the high-throughput analogs. Solutions to these difficult problems will result only from extended efforts to develop the needed measurement methods and the companion standards, calibration procedures, and measurement control programs.

More operational experience with dynamic materials balancing and high-precision bulk-measurement technology must be accumulated through carefully planned evaluations and demonstrations. Bulk-measurement improvements are critical for the implementation of classical and dynamic materials accounting concepts at commercial-scale reprocessing facilities. Future evaluations must address protracted performance in high radiation fields, including calibration stability, on-line calibration capability, and the distinction between random and systematic error effects under normal processing operations. Dynamic materials balancing hinges on the ability to estimate the in-process inventory in continuous processes. Experiments and demonstrations emphasizing the performance and reliability of the in-plant measurement instrumentation and the validity of the in-process inventory estimates are essential to translate this concept into reality.

Advanced safeguards instrumentation has been made only marginally palatable to process operators, who have historically viewed safeguards as an overlay of necessary evils. Consequently, the utility of safeguards information to plant operators for process control must be more fully demonstrated. It is merely the way measurement data are combined and analyzed that makes the information useful to the safeguards authorities as opposed to the process operators. Perhaps, it is a concomitant burden of the safeguards developers to demonstrate that the safeguards information can be used to operate and control the process.

We have selected prominent measurement needs for tomorrow's commercial-scale facilities and highlighted the promising trends in measurement technology development likely to provide solutions to these needs. Even from this cursory overview, it is evident that the scientific and engineering challenges facing us during the next decade emphasize application of measurement methods both individually and collectively to meet integral systems performance requirements. Past achievements in the development of nuclear materials measurement techniques now make it possible, and indeed mandatory, to embark on the new era--the systems approach to measurement technology development.

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