

Overview

Increased public awareness of radiation exposure and concern over possible health effects has elevated the need, both in the United States and abroad, to monitor all aspects of nuclear materials production and disposition. But, when compared with surveillance of industrial-scale non-nuclear operations, the task of monitoring nuclear operations is complicated by several factors, one of which is the simultaneous presence of hazardous and radioactive constituents in the products and production wastes. The scope of nuclear facility operations, which encompasses: (1) processing of irradiated and unirradiated feedstocks, (2) worker dosimetry, (3) waste management, (4) environmental surveillance, (5) decontamination and remediation, and (6) decommissioning, also creates a very high demand for characterization, especially with respect to radiochemical analyses.

Despite the fact that the United States Department of Energy (DOE) is changing the mission of many facilities from defense-related nuclear materials production to site remediation and monitoring, the need to fully characterize wastes and environmental samples, combined with the need to monitor worker radiation exposure by means of internal dosimetry (that is, bioassay), continues to increase the demand for radioisotope determinations. Active nuclear facilities in the United States and elsewhere are strongly emphasizing these determinations, and they are concurrently demanding better and faster analysis techniques to assure the quality of the materials that they supply for nuclear energy production and other nuclear technologies. These factors have conspired to increase radioanalytical demand significantly; for example, the DOE Office of Environmental Management (DOE-EM) has estimated that 321 000 samples may be collected in fiscal year 1995, generating requests for as many as 910 000 radiochemical measurements [1]. These measurements are being made solely to support nationwide DOE initiatives in nuclear waste management and nuclear facility cleanup; thus, the overall demand for radiochemical analyses (especially worldwide) will certainly be greater than this owing to the continued production and handling of nuclear materials!

Traditional Radionuclide Determinations and New Technologies

Materials to be analyzed in support of nuclear operations include bulk nuclear materials, homogeneous and heterogeneous wastes from production and decontamination/remediation (that is, radioactive and hazardous wastes, or both), air filters, soil, ground and surface water, biota, and bioassay (internal dosimetry) samples. Radiation levels in these materials may vary from >100 R in some nuclear processing wastes to background levels in many environmental and bioassay samples, but detailed knowledge of the radioisotopic composition in all of these materials is necessary to facilitate informed decisions on product quality, worker exposure, waste treatment and containment, site remediation, decontamination, and decommissioning.

Nonradiometric techniques have been employed in some situations to determine radionuclides; for example, thermal ionization mass spectrometry (TIMS) has been used to determine the isotopic composition of several actinides, and kinetic phosphorimetry has been used to determine undifferentiated (total) uranium. However, analysts have historically relied upon radiometric techniques, that is, α spectrometry, γ spectroscopy, scintillation, and proportional counting, to perform most radionuclide determinations. Attendant with these

techniques (gamma spectroscopy excepted) are painstaking chemical separations that are necessary if radiometric interferences are to be avoided. Also significant is the limiting influence of the analyte (or, more specifically, the analyte half-life) upon method detection limits. Under this limitation, "best" detection limits are especially difficult to achieve with long-lived radionuclides and can only be attained when large sample size, high chemical yield, and long counting period are combined.

Long-lived radionuclides, for example, ^{239}Pu and ^{235}U have played a significant role in the nuclear age, and as such, their determination will continue to be important as nuclear facilities are decommissioned. However, the analytical methodology used for these determinations are likely to change significantly over the next several years, as concerns over radioanalytical turnaround time and cost have stimulated research into new radioanalytical techniques and procedures. Many alternatives to radiometry are being studied [2-4], however, one of the most promising techniques for radionuclide determinations appears to be inductively coupled plasma-mass spectrometry (ICP-MS). This technique is in its 13th year of commercial availability, and there are numerous reviews [5,6], serials [7-9], and monographs [10,11] that describe, in detail, instrumental capabilities and performance. But, despite this wealth of knowledge, and despite the fact that the first ICP-MS was (by coincidence) developed at a DOE laboratory [12], routine use of ICP-MS in radionuclide determinations has been slow to develop.

ICP-MS and Radionuclide Determinations

This special technical publication (STP) documents the proceedings of the 1994 symposium on Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations. This symposium was held on 13 and 14 October, 1994 in Gatlinburg, Tennessee following the 35th ORNL/DOE conference on Analytical Chemistry in Energy Technology. The symposium was a continuation of work started by the Plasma Spectroscopy task group of ASTM Subcommittee C26.05 on Nuclear Fuel Cycle Test Methods, but it is important to note that the DOE Office of Transportation, Emergency Management, and Analytical Services (EM-76) was also involved in the genesis of the symposium. All of the contributions to this STP, except the paper by Noé and Hérès, were presented at the Gatlinburg symposium. Dr. Noe was invited to the symposium but was unable to attend; however, he graciously agreed to submit a manuscript for publication. Two other symposium presentations, including the keynote address by Professor Sam Houk of Iowa State University, were not available for publication.

This collection of twelve papers presents a "snapshot" of the ICP-MS techniques and procedures that are being developed for the purpose of radionuclide determinations. Analysts and project managers (that is, ICP-MS users and clients) are the target audience of this publication, as they will provide the impetus for further research and eventual integration of ICP-MS techniques into the service analytical laboratory. The needs of this audience are addressed by intentionally presenting a combination of on-going research and established procedures that cover a wide selection of matrices, sample radioactivity, analytes, and data objectives. For reasons of continuity, the papers have been roughly arranged into four groups: (1) applications in nuclear material production, (2) applications in high-level waste characterization, (3) applications in environmental monitoring and waste management, and (4) applications in internal dosimetry and health protection. The technical content of these groups are summarized below.

Applications in Nuclear Material Production

The two papers in this section (both from the United Kingdom) describe the determination of radionuclide concentrations and isotope ratios in enriched uranium products. In the

first contribution, ICP-MS and various preparative techniques were evaluated for the determination of ^{99}Tc in process samples and product uranium compounds from a uranium enrichment plant. In the other paper, a novel magnetic sector ICP-MS having multiple detection channels was used to determine $^{235}\text{U}/^{238}\text{U}$ in hydrolyzed uranium hexafluoride. The precision of these measurements was equal or superior to that achieved using TIMS, despite the fact that the ICP-MS analyses were completed in 80% less time.

Applications in High-Level Waste Characterization

The three papers in this section (one from France and two from former DOE plutonium production sites) describe ICP-MS techniques that can be used to support high-level waste processing, waste stabilization, and waste acceptance criteria for long-term storage. The first of these papers describes the determination of transuranium elements and fission products present in reprocessing waste from civilian and defense nuclear facilities. New preparative techniques for the determination of Tc and radioiodine are described. In the second paper, ion chromatography (IC) coupled with ICP-MS is used to separate and detect 20 radionuclides in radioactive tank waste samples. Automated IC separations using shielded instrumentation allowed determination of 47 elements and 160 radionuclides in a single run. The remaining paper describes microwave and conventional acid digestions that may be used to dissolve high-level tank waste samples prior to ICP-MS determination of α and γ emitting isotopes. Data reduction techniques that minimize spectral interferences are also described.

Applications in Environmental Monitoring and Waste Management

The papers in this section (one from the United Kingdom and four from the United States) describe established procedures and current research directed toward the determination of radionuclides for environmental monitoring and waste management. The first paper describes a high-sensitivity quadrupole ICP-MS instrument that can achieve pg/L (ppq) detection limits for actinides and fission products using conventional pneumatic nebulization techniques. Precise determinations of lead and silver isotope ratios at $\mu\text{g/L}$ (ppb) elemental concentrations are also described. The second paper compares ICP-MS determination of total uranium and uranium isotopic distributions in mixed waste materials with TIMS and fluorimetric determinations. The data indicate that ICP-MS determination of total U at $\mu\text{g/L}$ levels are comparable to fluorimetric determinations, while the isotopic determinations by ICP-MS are suitable for control of ^{235}U in waste storage and treatment operations.

The need to report vanishingly small radionuclide concentrations has driven development of sample preconcentration, elemental separation, and matrix elimination techniques that are designed specifically for ICP-MS measurements. Several of these efforts are described in the remainder of this section. In the first of these papers, an innovative combination of stripping voltammetry and ICP-MS is reported. This combination permits selective concentration and subsequent determination of Tl and U isotopes at ng/L (ppt) concentrations. The other papers describe the use of extraction chromatography with ICP-MS for actinide preconcentration and determination. In the first of these papers, preconcentration, matrix elimination, and determination of actinides in soil is achieved using flow injection coupled directly with ICP-MS. This technique can determine environmental levels of Th, U, and Pu isotopes faster and at lower cost than traditional radiochemical methods. The final paper describes off-line use of column chromatography for matrix elimination and analyte concentration prior to determination of Th and U isotopes. The procedure is used routinely to support remediation and decommissioning activities at a former DOE nuclear site.

Applications in Internal Dosimetry and Health Protection

The first paper of this section presents data from a long-term study of U isotope distributions in airborne particulates. Isotope ratios were determined with ICP-MS instead of TIMS. Using as little as 10 ng of uranium, ICP-MS determinations of $^{235}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{238}\text{U}$ met data quality objectives, while cost and turnaround time were reduced. The final paper describes the routine use of ICP-MS to monitor worker exposure to uranium at a gaseous diffusion plant. This method has been in routine use for some time, and has proven reliable for the determination of total uranium and $^{235}\text{U}/^{238}\text{U}$ in worker urine.

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