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Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations

Roy W. Morrow
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Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations: Second Volume

Roy W. Morrow and Jeffrey S. Crain, Editors

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Foreword

This publication, *Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations: Second Volume,* contains papers presented at "The Second Symposium on Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations," which was held 3-4 March, 1998 in New Orleans, Louisiana, during the 1998 Pittsburgh Conference and Exposition. The symposium was sponsored by ASTM Committee C–26 on the Nuclear Fuel Cycle and the 1998 Pittsburgh Conference Program Committee. Roy W. Morrow of Lockheed Martin Energy Systems (Oak Ridge, Tennessee) and Jeffrey S. Crain of Argonne National Laboratory (Argonne, Illinois) and Union Carbide Corporation (South Charleston, West Virginia) organized and presided over the symposium and are co-editors of this special technical publication.

Dedication—Velmer Arthur Fassel

Distinguished Professor of Chemistry, Iowa State University

The Society for Applied Spectroscopy Gold Medal Award, 1964
The Pittsburgh Spectroscopy Award, 1969 (Spectroscopy Society of Pittsburgh)
The Maurice F. Hasler Award, 1971 (Spectroscopy Society of Pittsburgh)
The American Chemical Society (ACS) Award in Analytical Chemistry, 1979
The ACS Division of Analytical Chemistry Award in Chemical Instrumentation, 1983
The Lester W. Strock Award, 1986 (Society for Applied Spectroscopy)
The ACS Division of Analytical Chemistry Award in Spectrochemical Analysis, 1988
The Pittsburgh Analytical Chemistry Award, 1995
(Society for Analytical Chemists of Pittsburgh)

On March 4, 1998, Professor Velmar Fassel passed away, leaving behind a legacy of scientific achievement which has—at the very least—shaped the development of analytical atomic spectroscopy during the latter part of this century. Starting in the 1960s, Professor Fassel and his co-workers set the course leading to development of analytical ICP emission spectroscopy, and in the 1970s, they were equally successful in developing and demonstrating the first ICP mass spectrometer. Without question, Fassel's work serves as a standard against which other analytical spectroscopists are judged, and it is likely that this will continue to be so, even in the next century.

For resons known only to a greater power, Professor Fassel's passing coincided with the symposium described in this Special Technical Publication. Without his many years of dedication and innovation, the technology underlying this symposium would not have existed; therefore, it is with great respect and appreciation that we dedicate this publication to his memory.

Contents

Overview—R. W. MORROW AND J. S. CRAIN vii

APPLICATIONS OF ICP-MS IN THE NUCLEAR FUEL CYCLE

Uranium Isotope Measurements by Quadrupole ICP-MS for Process Monitoring of Enrichment—TIMOTHY A. POLICKE, ROBERT N. BOLIN, AND TERRY L. HARRIS 3

A Study of Isotopic Homogeneity in "Blended Uranium" Using ICP-MS—JEFFREY S. CRAIN 16

High Precision and High Accuracy Isotopic Measurement of Uranium Using Lead and Thorium Calibration Solutions by Inductively Coupled Plasma-Multiple Collector-Mass Spectrometry—IAN BOWEN, ANDREW J. WALDER, TOM HODGSON, AND R. R. PARRISH 22

Actinide, Elemental, and Fission Product Measurements by ICPMS at the Savannah River Site—LAURA L. TOVO, JOSEPH W. CLYMIRE, WILLIAM T. BOYCE, AND W. FRANK KINARD 32

Evaluation of Nebulizer Performance within the ICP-MS Measurement System for Analysis of SRS Radiological Waste Tank Simulated Solutions—VERNON D. JONES 41

Determination of Long-Lived Beta Emitters in Nuclear Waste by Inductively Coupled Plasma-Mass Spectrometry—PHILIPPE G. BIENVENU, ERIC A. BROCHARD, AND EMMANUEL A. EXCOFFIER 51

Determination of Technetium-99, Neptunium-237 and Isotopes of Thorium in Uranyl Nitrate Solutions from a Reprocessing Plant, Using Double-Focusing ICP-MS—BERNARD MITTERRAND, PIERRE LEPROVOST, JACQUES DELAUNAY, AND ALAIN M. VIAN 64

APPLICATIONS OF ICP-MS IN HEALTH AND ENVIRONMENTAL MONITORING

Evaluation of Chelation Preconcentration for the Determination of Actinide Elements by Flow Injection ICP-MS—E. HYWEL EVANS, JASON B. TRUSCOTT, LEE BROMLEY, PHIL JONES, JUSTINE TURNER, AND BEN E. FAIRMAN 79

Determination of Uranium in Clinical and Environmental Samples by FIAS-ICPMS—ZEEV KARPAS, AVRAHAM LORBER, LUDWIK HALICZ, AND ITAI GAVRIELI 89

^{99}Tc Bioassay: A Direct Comparison of Liquid Scintillation Radiation Detection and ICP-MS Mass Detection of the ^{99}Tc Isotope—LINDA A. LEWIS AND GEORGE K. SCHWEITZER 99

Determination of Radionuclides in Biological Fluids Using a High Resolution ICP-MS in Low Resolution Mode—CHRISTOPHER J. PICKFORD, JANICE HAINES, RUTH HEARN, AND JOHN McAUGHEY 111

High-Precision Determination of $^{234}U/^{238}U$ Activity Ratios in Natural Waters and Carbonates by ICPMS—MICHAEL E. KETTERER AND CHRISTOPHER J. KHOUREY 120

Isotope Ratios of Uranium Using High Resolution Inductively Coupled Plasma-Mass Spectrometry (ICP–MS)—RUTH HEARN AND HEIKO WILDNER 137

Overview

As the world moves inexorably toward the 21st century, the global community of scientists and engineers can look back proudly upon the achievements of this century. Diseases thought to be intractable in the latter century, e.g., polio and smallpox, were cured, and technologies that were inconceivable to the great 19th century thinkers, e.g., microprocessors and lasers, were developed. The development of controlled nuclear fission, and the ongoing efforts to harness nuclear fusion, certainly fall within the latter category; however, for reasons political and environmental, not only must we look to the future of these energy sources, we must also look at the legacy of their development.

Even in the next century, Chernobyl, Three Mile Island, and Hanford will likely serve as object lessons of nuclear technology gone awry, and it is equally likely that the technological problems created by these disasters will challenge future generations of scientists and engineers. The threat of nuclear proliferation (as exemplified by the recent Indian and Pakistani nuclear weapons tests) will also remain, as will the problems surrounding secure storage of nuclear wastes—whether of military or civilian origin. But, despite these problems, many nations will continue to rely upon nuclear energy; therefore, at the very least, development of supporting technologies must continue apace to match the level of oversight demanded by governments and the public at large.

Chemical metrology (aka analytical chemistry) will almost certainly remain as one of the key supporting technologies for nuclear energy production, waste management, and environmental restoration. A number of significant discoveries in analytical chemistry, e.g., development of solvent extractions and sulfonate cation exchange resins, came about as a consequence of early efforts to characterize nuclear materials, and as nuclear technologies have matured, so too have the supporting measurement techniques. Instruments have played a pivotal role in the maturation of these nuclear-related measurements, and this brings us to the focus of this special technical publication.

Even from its early conception [1], inductively coupled plasma-mass spectrometry (ICP-MS) was thought to be well-suited to the unique measurement problems facing the nuclear industry. These thoughts were well-founded; indeed, one might consider it unusual if a modern nuclear research center did not have access to one or more ICP mass spectrometers (quadrupole or otherwise). However, as ICP-MS has matured, improvements in sensitivity and precision have made possible measurements that were inconceivable to the "founding fathers" of the technology. Therefore, there is a periodic need to gather information and obatin a "snapshot in time" of the technology and its applications in nuclear energy.

In March of 1998, a symoposium entitled "Applications of ICP-MS to Radionuclide Determinations" was convened in conjunction with the 1998 Pittsburgh Conference and Exhibition to obtain the aforementioned "snapshot in time." The 1998 symposium was the second of its kind—the first was held in 1994 at the ORNL/DOE Conference on Analytical Chemistry in Energy Technology [2]. However, unlike the first symposium, the second was an international event in which speakers from the United States, Europe, and the Middle East described new developments in ICP-MS relevant to the nuclear energy community. The papers presented at the 1998 symposium are published herein, and in the balance of this overview, we shall summarize the innovative techniques described by the presenters.

Applications of ICP-MS in the Nuclear Fuel Cycle

Papers by T. A. Policke et al. and J. S. Crain describe the use of ICP-MS for the assessment of isotopic composition in uranium products. The work by Policke examines the performance of quadrupole ICP-MS over a broad range of uranium enrichments, whereas Crain focuses primarily upon uranium down-blended to reactor-grade enrichment. Both papers describe methods that support uranium blending operations, and it is important to note that in the foreseeable future these operations will likely serve as a primary means of reducing highly-enriched (i.e., weapons grade) uranium inventories in the United States and elsewhere.

I. Bowen et al. describe the continued refinement of ICP multicollector MC (a magnetic sector mass spectrometer) for the precise and accurate determination of uranium isotope ratios. In their study, thorium or lead was used as an internal reference for the calibration of uranium isotope ratios. Using this method, isotope ratio precision was easily on par with thermal ionization MS (TIMS); however, sample throughput was four to five times greater than that which is typical of TIMS. This methodology may one day find equal application in characterization of nuclear and environmental media.

Papers by L. L. Tovo et al. and V. D. Jones describe applications of ICP-MS at the Savannah River Site (SRS) near Aiken, SC. Tovo and co-workers describe lessons learned while operating one of the first radiologically-contained ICP mass spectrometers (VG PlasmaQuad I, serial no. 4) in support of activities ranging from environmental monitoring to defense waste vitrification. Jones' work focuses more closely upon a specific application: characterization of high-level liquid waste. The effects of dissolved solids, which can approach 25% in the sample matrix, were studied, with particular attention paid toward nebulizer performance and ruggedness. These papers present a very clear picture of the challenges that face analytical chemists at nuclear facilities, particularly as we remediate the chemical and radiological legacy of nuclear weapons production.

Papers by P. G. Bienvenu et al. and B. Mitterrand et al. describe applications of ICP-MS toward nuclear waste management in France. Bienvenue describes the determination of long-lived β emitters (e.g., ^{135}Cs) in waste materials destined for long-term storage. Compared with traditional methods (such as liquid scintillation), ICP-MS required fewer preparative steps, thus simplifying the determination of these important radionuclides. Mitterrand describes the determination of ^{99}Tc, ^{237}Np and Th isotopes in uranyl nitrate solutions destined for reprocessing. A double-focusing, high-resolution ICP mass spectrometer was used to increase measurement sensitivity (in low resolution mode) or reduce spectral interferences (in high resolution mode). Overall, these papers present an inside look at French waste management policies, which are, in many respects, more consistent with modern environmental philosophy (e. g., "recycle and reuse") than are the United States' policies.

Applications of ICP-MS in Health and Environmental Monitoring

E. H. Evans and co-workers describe the development of on-line sample processing techniques for the determination of actinides in natural waters. With matrix elimination and analyte preconcentration, method detection limits in the pg range were achieved for Th and U; however, these were blank-limited, and yet lower limits (fg range) would be expected for anthropogenic actinides (Np, Pu, and Am). Techniques like those described by the authors underlie many ICP-MS methods for the determination of radionuclides in natural media, as exemplified by Z. Karpas et al. in their study of uranium in clinical and environmental media.

Like Karpas and co-workers, L. A. Lewis and G. K. Schweitzer, and C. J. Pickford et al. describe techniques for the determination of radionuclides in clinical media. Lewis and

Schweitzer studied the determination of ^{99}Tc in urine, and found that by using extraction chromatography for sample clean-up and analyte concentration, ICP-MS data were equally accurate and more precise than data from liquid scintillation. Pickford and co-workers obviated the need to concentrate analytes by virtue of using a double-focusing sector ICP-MS in its low resolution (high sensitivity) mode. With ultrasonic nebulization, instrument detection limits were less than 1 pg/L for 244Pu; however, several unexpected spectral interferences were encounted, and these required development of specialized preparative methods. Among other things, these papers demonstrate that, in challenging applications, even the most powerful instruments require good chemistry "up front" to produce meaningful data.

Papers by M. J. Ketterer and C. J. Khourey, along with R. Hearn and H. Wildner, describe ICP–MS methods for the characterization of geological media. Ketterer and Khourey used extraction chromatography and recirculating nebulization to precisely determine the $^{234}U/^{238}U$ mass ratio in natural waters and carbonate rocks. For 5 to 25 μg U, isotope ratio uncertainties were on the order of 0.2 to 0.5% RSD, which is roughly consistent with that obtained by TIMS using 100 ng U or less. In their study, Hearn and Wildner used the high sensitivity of double focusing sector ICP-MS (run in its low resolution mode) combined with ultrasonic nebulization to determine isotope ratios for several purposes, including assessment of past nuclear activity ("nuclear forensics") and geochronometry. Both of these papers indicated that, in isotope ratio determinations, quadrupole and double-focusing sector ICP-MS are outperformed by TIMS; however, it is equally obvious that ICP-MS is more productive than TIMS. Thus, in certain applications (e.g., environmental surveys), one can expect that ICP-MS will, in the future, serve as a tool by which samples may be screened and selected for slower and more expensive TIMS measurements.

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