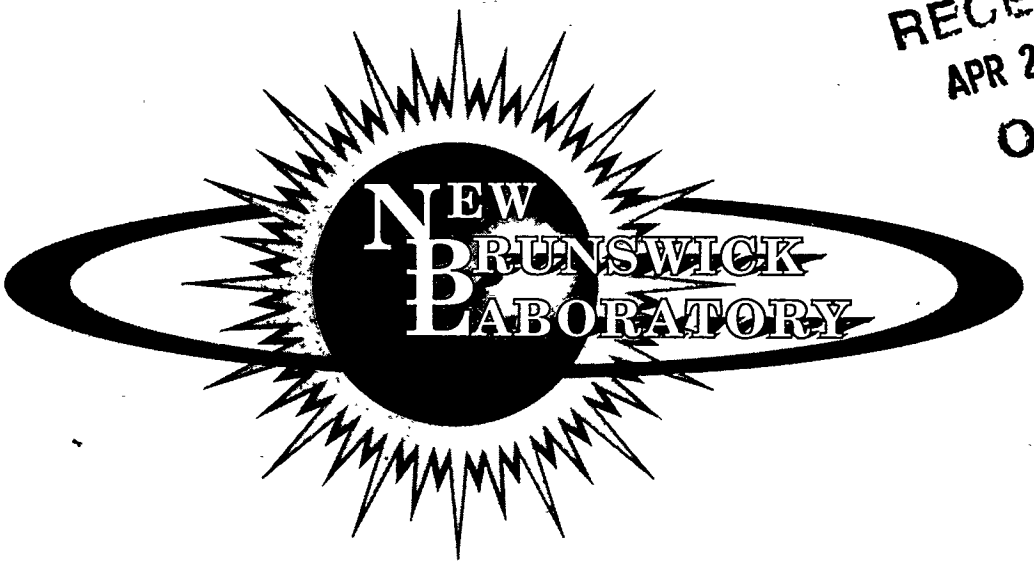
NBL-335
MARCH 1996

PROGRESS REPORT



OCTOBER 1994
THROUGH
SEPTEMBER 1995

U.S. DEPARTMENT OF ENERGY • CHICAGO OPERATIONS OFFICE • ARGONNE, ILLINOIS

NBL-335

U. S. DEPARTMENT OF ENERGY

CHICAGO OPERATIONS OFFICE

NEW BRUNSWICK LABORATORY

H. RODNEY MARTIN, ACTING DIRECTOR

PROGRESS REPORT

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DOE RESEARCH AND DEVELOPMENT REPORT

MARCH 1996

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MISSION

The mission of the New Brunswick Laboratory of the U. S. Department of Energy (DOE) is to serve as the National Certifying Authority for nuclear reference materials and to provide an independent Federal technical staff and laboratory resource performing nuclear material measurement, safeguards, and non-proliferation functions in support of multiple program sponsors.

EXECUTIVE SUMMARY

During FY 95 New Brunswick Laboratory (NBL) continued activities to enhance awareness of NBL's skills and capabilities, and initiated a variety of actions to improve communications and respond to the needs of the global nuclear community. In carrying out these initiatives, NBL published a brochure describing it's programs and operations. NBL also began development of a business management plan which focuses on analysis of program objectives, identification of issues, and mission accomplishment through integration of multi-program tasks. Implementation has resulted in a variety of new directions and changes in most of the functional program areas. Aggressive actions were taken to assure program products met prioritized customer requirements and to integrate requirements from multi-program sponsors. In addition, NBL has continued to identify and evaluate nuclear community issues and directions in order to better match services/projects to changing DOE requirements. The Laboratory has also continued an aggressive employee development program, with particular emphasis on outside technical areas and on team performance and customer responsiveness.

This annual report describes accomplishments achieved in carrying out NBL's assigned missions. Details of completed projects are reported in separate topical reports or as open-literature publications.

Safeguards Assistance

NBL technical expertise is utilized to provide safeguards assistance to Headquarters (HQ), to Operations Offices, to contractor facilities when requested by their Operations Offices, and to other customers. During FY 95, six NBL personnel participated in four periodic Operations Office surveys. These reviews were impacted temporarily during a moratorium on business-line reviews but are projected to increase substantially during FY 96 as Operations Offices downsize and their technical safeguards experience declines. Three NBL personnel also provided Nuclear Regulatory Commission (NRC) inspection assistance and trip reports for five trips to four licensees, including a special request for a sampling plan for "Sapphire" uranium materials. Site-specific assistance was provided to facilities through the Albuquerque, Oak Ridge and Savannah River Operations Offices. In addition, NBL continued to assist the Central Training Academy (CTA) with course preparation and with presentation of Material Control and Accountability (MC&A) course lectures.

An Inventory Performance Test Program proposed by NBL was approved and issued by the Office of Safeguards and Security (OSS) in December 1994. Subsequently, NBL personnel participated in an OSS sponsored performance testing workshop where the NBL Inventory Performance Test Program was discussed and provided to participants. Other HQ assistance activities included drafting performance

oriented MC&A criteria based on safeguards and security standards and criteria; providing review, comment, input for a variety of MC&A policies, plans and issues; and participating in a HQ/On-Site Inspection Agency mock Chemical Warfare Convention inspection. NBL personnel continued to support International Safeguards projects through Office of Nonproliferation and National Security (NN)-40 and Office of Nuclear Energy (NE)-30 for Russia, Ukraine, Kazakhstan, Uzbekistan, and for the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC).

Reference Materials

NBL, as the U. S. Government's certifying authority for nuclear reference materials, provides Certified Reference Materials (CRMs) traceable to a nationally accepted, internationally compatible reference base for calibration and standardization of nuclear material measurements. During FY 95, extensive efforts were started to better assess standards needs of the nuclear community and to respond through changes in program direction. Specific actions included going to smaller quantities of ready-to-use ampulated nitrate solutions for some replacement CRMs which reduces shipping problems and diminishes risks of contamination and instability; initiation of projects to jointly prepare environmental standards with other laboratories for International Atomic Energy Agency (IAEA) nonproliferation monitoring; obtaining funding from NRC for preparation of standards needed by licensees; and establishing a design and beginning preparation of nondestructive assay (NDA) standards for Oak Ridge Y-12 uranium waste assay. In addition, support was provided to Westinghouse Hanford for shipment of PuO_2 inspection samples to the IAEA and to EG&G's Special Technologies Laboratory by providing uranium materials for use in an interagency exercise.

In FY 95, 461 units of 41 different CRMs (60 domestic and 31 foreign orders) were sold for a total cost of $133,691.50. In addition, uranium NDA standards for the Y-12 site valued at $95,401 were fabricated. Other items of note included:

- Reference material projects were completed or are underway involving the following CRMs: U0002-A, U007, U010-A, U015-A, U050-A, U930-D, CRM 42A, CRM 125-A, and CRM 145.

- The design of the NDA standards provides small packages that can be utilized with site-specific containers and matrices. This approach avoids having to create special standards for each individual site.

- A re-costing of historical reference materials was completed and provisions for an annual adjustment to each reference material price were implemented.

- The CRM catalog, Material Safety Data Sheets, and most Certificates of Analysis were made available on the NBL Local Area Network (LAN). This permits in-house revision, printing and issuance of these materials on an as needed basis.

- Discussions were held with NN-40 personnel to pursue an improved approval process for foreign orders. Currently some foreign orders for reference materials may be held up for years before approval is received to ship the material.

- Limitations on material quantities at NBL require some CRMs to be fabricated at other locations. This may sometimes result in not achieving controls required for reference material certification.

- Shipping constraints, particularly limited availability of certified containers, continues to impede sales and certification efforts.

Measurement Evaluation

NBL manages interlaboratory measurement evaluation programs to provide independent validation of facility nuclear material measurement capabilities and performance. The NBL Safeguards Measurement Evaluation (SME) program includes preparation, characterization, packaging and distribution of samples to participating laboratories. The receipt, recording, statistical evaluation and reporting of the measurement results from the participating laboratories are the products of the Program. These results provide facility and oversight organizations with prompt identification of whether facility measurement programs are in control, measurement comparability between participating laboratories and with international target values, and a basis for evaluating measurement performance as a source for inventory anomalies. During FY 95, SME results indicate that all participating facilities are performing safeguards measurements within the target values for bias for their respective methods of analysis.

Actions were also initiated or planned to upgrade the NBL SME program during FY 95. Specific Highlights included:

- A new database application that streamlines data entry, statistical analysis, and graphics and report generation was developed to replace an outdated system . Future planned enhancements include direct data entry and inquiry by participating facilities.

- An agreement was reached with the NRC to include selected NRC licensees in the program beginning in FY 96. Expanded participation by the Former Soviet Union (FSU) and other international organizations is being explored.

- A new solution prepared from a plutonium isotopic CRM was added during FY 95; plans are to distribute materials to plutonium participants to be analyzed for total plutonium in FY 96.

- Plans are being developed to incorporate uranium NDA gamma standards into the SME program.

Measurement Development

Most Measurement Development Program projects in recent years have centered on increasing the efficiency and effectiveness of measurement methods that primarily support the Reference Materials, SME, and Measurement Services programs. Other development projects focused on waste minimization/pollution prevention, and upgrading and replacing obsolete analytical instrumentation. These projects are necessary for NBL to function as a productive state-of-the-art analytical laboratory.

Highlights from the Measurement Development Program are summarized below:

- Two Environmental Management (EM) funded projects yielded methods which reduce waste. Pu isotope dilution mass spectrometry generates less waste than the current assay method and, additionally, the smaller analysis quantities reduce interfacility shipping problems. The automated coulometric determination of uranium method can eliminate the creation of a mixed waste resulting from the present NBL titrimetric method.

- Development of a laser kinetic phosphorimetric method for analysis of very low levels of uranium in solution was completed and implemented in FY 95. This method will be used for analysis of NBL waste streams and other low level analyses.

- A procedure was developed for analysis of impurities in samples via x-ray fluorescence spectrometry to provide information on sample composition prior to destructive analysis.

- Analytical Instrumentation progress included installation of a new Inductively Coupled Plasma Atomic Emissions Spectrometer (ICP-AES) and completion of glovebox installation for the Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

- Procedures for the INSpector portable NDA system were developed and utilized for in-field NDA and hold-up measurements.

Measurement Services

NBL, as the Government's Nuclear Material Measurements and Standards Laboratory, serves as the Federal laboratory authority for DOE and provides measurement services on a contractual basis for the NRC. A primary function of this program is to support the Reference Material and SME programs. During FY 95, NBL received 96 uranium samples and 16 plutonium samples for analysis. Analytical methods as required, such as titrimetry, gamma spectrometry, and mass spectrometry were performed on these samples.

NBL participates in the SME program to evaluate the stability and integrity of SME materials and to meet quality assurance (QA) requirements. There were 50 uranium and 16 plutonium samples received for analysis under the SME program. NBL also participated in the Institute for Reference Materials and Measurements (IRMM) Regular European Interlaboratory Evaluation Program (REIMEP) uranium exchanges.

The NRC submitted a total of 66 uranium samples for inventory verification during FY 95.

NBL provided measurement services to the ABACC by performing isotopic analyses to characterize a U_3O_8 material to be used as a secondary standard in the agency's sample exchange program.

SAFEGUARDS ASSISTANCE PROGRAM

M. A. Legel and W. G. Mitchell

Summary

A goal for the Safeguards Assistance Program at the New Brunswick Laboratory is to optimize the utilization of NBL's technical expertise in support of DOE's nuclear material measurement, safeguards and non-proliferation missions. Progress towards this goal was attained through the following activities: Safeguards and Security Information Management System (SSIMS) database access, cataloging of Program resources, expanded training opportunities, and use of new survey participants to gain experience in periodic surveys. During FY 95, six NBL personnel participated in four periodic surveys with two operations offices. Three NBL personnel provided NRC inspection assistance and trip reports for five trips to four licensees during this year, including a special request for a sampling plan for "Operation Sapphire" uranium materials. An Inventory Performance Test Program proposed by NBL was approved by the Office of Safeguards and Security in December 1994. NBL personnel participated in an Office of Safeguards and Security sponsored workshop at the Central Training Academy which covered performance testing. The incorporation of NBL measurement performance tests into facilities' performance assurance programs was discussed and copies were issued to participants as well as Operations Offices. HQ assistance activities included drafting performance oriented criteria for MC&A based on the safeguards and security standards and criteria, providing input for an annual assessment of MC&A policy, participating in a mock Chemical Warfare Convention inspection, in addition to policy review/comment for draft DOE Orders and specific nuclear material storage issues. New Brunswick Laboratory personnel provided assistance to the Central Training Academy with preparation of lesson plans and presentation as adjunct faculty for CTA MC&A course lectures. Site-specific assistance in the area of NDA and uranium isotope dilution mass spectrometry was provided to facilities through the Oak Ridge and Savannah River Operations Offices. NBL personnel continued to support International Safeguards projects through NN-40, NN-44 and NE-30 for Russia, Ukraine, Kazakstan, Uzbekistan, and for ABACC.

Program Administration

The Safeguards Assistance Program at the New Brunswick Laboratory works to optimize the use of NBL's technical expertise. Support of DOE missions was provided by NBL expert's work with the SSIMS database, resource cataloging, training opportunity expansion, and use of new NBL survey participants. A Central Training Academy course, MCA-103, "Introduction to Performance Testing," was brought to the Chicago area in October 1994 and twelve NBL students attended. NBL personnel have taken advantage of local training workshops and training courses such as Survey Procedures Workshop, (PPM200D), Detecting Violent Behavior in the Workplace, and the CD-ROM training, "Introduction to MC&A," MCA 101-D, offered through the Central Training Academy. Other applicable training courses attended by NBL safeguards cadre personnel included a Canberra seminar on Radwaste characterization with NDA instrumentation, and MC&A

courses, MCA 111, "Nuclear Materials Accounting," PHY 230, "Facility Survey Team Leader," MCA 150, "Materials Control and Accountability Inspection Procedures, and MCA 343, "Gamma-Ray Spectroscopy for Nuclear Materials Accounting." A workshop was held for safeguards assistance cadre members to discuss new program resources and the operation of a Canberra InSpector instrument for NDA measurements. Additional workshops are planned to discuss other issues, such as survey preparation, report writing, performance tests, and ongoing NBL assistance activities. Information exchange among program participants will allow for a consistent approach by all team members to common issues among various Operations Offices and contractor facilities. Development of a site contact and training database was initiated to track safeguards cadre activities and training. Regular access to the Safeguards Document Retrieval System (SDRS), now available only through the Central Training Academy's TRAINERNET system, was made to keep NBL resources current with DOE-HQ policy and guidance publications.

Operations Office Periodic Survey Assistance

As a technical extension of OSS, NBL provided MC&A expertise to the DOE operations offices for periodic surveys of facilities. During FY 95, six NBL personnel participated in four periodic surveys with two operations offices, Richland and Oak Ridge Operations Offices. Periodic survey assistance to Operations Offices was provided by Dr. Usha Narayanan, Dr. Paul Croatto, Ms. M. Irene Spaletto, Mr. Peter Mason, Mr. Anthony Traina, and Dr. Wanda Mitchell. The MC&A deficiencies identified by NBL personnel during these reviews are included in the SSIMS database review which was included in the annual policy assessment document prepared for NN-512.4. Assistance activities were impacted since Safeguards and Security was included temporarily in the moratorium on business-line reviews imposed by DOE while pilot business management reviews were initiated.

Other NBL Safeguards Assistance

The CH classification officer, Mrs. Colleen Gradle, marked declassified documents, reviewed foreign travel reports and provided classification assistance as requested. That responsibility has now transferred back to other personnel in the Chicago Operations Office. An NRC Statement of Work for FY 95-99 funding was negotiated and finalized in April 1995. The Safeguards Assistance Program will continue to provide NBL personnel for three to four trips annually for NRC inspections. Three NBL personnel provided NRC inspection assistance and trip reports for five trips to four licensees during this year, including a special request for a sampling plan for "Operation Sapphire" uranium materials received at Babcock & Wilcox Nuclear Naval Fuel Division (B&W NNFD) for processing. NRC Inspection assistance was provided by Dr. David Baran, Mr. Robert Oldham and Dr. H. Rodney Martin.

Performance Testing

An Inventory Performance Test (IPT) Program proposed by NBL was approved by the Office of Safeguards and Security in December 1994. The Program was proposed to identify potential discrepancies due to incorrect or inaccurate accountability measurement uncertainty in DOE Special Nuclear Material (SNM) inventories which may be identified by future outside agency inspections. Where appropriate, NBL will assist the sites with improvement of measurement methods or in preparing traceable, representative standards when requested by the Operations Office. The Program was discussed at the Material Control and Accountability Representatives meeting. Mr. Robert Oldham and Ms. Margaret Legel attended an Office of Safeguards and Security sponsored workshop at the Central Training Academy in April 1995. The incorporation of NBL measurement performance tests into facilities' performance assurance programs was discussed. As follow up, updated copies of the performance tests were distributed to the participants as well as Operations Offices. Dr. David Baran utilized NBL's portable NDA system, a Canberra InSpector, a gamma-ray spectrometric instrument at an NRC inspection. As further experience is obtained and training is developed, a NBL measurement performance test can be developed and the equipment will be available for additional NBL assistance activities.

NBL Assistance to Headquarters

As part of its mission, NBL provided review and comment on MC&A policy documents as requested by the MC&A Branch, NN-512.4. The documents included DOE Order 5633.3B, "Material Control and Accountability;" DOE Order 5633.3B implementation guidance document, Standards and Criteria - Chapter IV; MC&A Format and Content Guide; DOE 5630.11C, "Safeguards and Security Programs;" DOE 5650.4, "Identification and Protection of UCNI;" Oak Ridge shipper/receiver agreement proposal for MC&A on the "Operation Sapphire" materials; and storage of plutonium in an Oak Ridge facility. NBL drafted performance orientated criteria for MC&A based on the Standards and Criteria and submitted information for an OSS annual policy assessment. Assistance was provided to NN-513 by NBL's Dr. Jeffrey Zebrowski as a team member for a mock Chemical Warfare Convention inspection team at the Lawrence Livermore National Laboratory. Three reviews were also completed for the Small Business Innovative Research (SBIR) program, which pertained to automated material control devices/mechanisms. In addition, NBL provided MC&A expertise for a material categorization and storage issue at Sandia National Laboratory at the request of NN-512.4.

Sampling plans and cost estimates were prepared and forwarded to NN-512.4 for proposed destructive analyses at NBL on the "Operation Sapphire" enriched uranium materials received from Kazakstan. Further

analyses were not performed before the materials were sent to an NRC licensee, Babcock & Wilcox Nuclear Naval Fuel Division. Further support from NBL for sampling and sample analysis support was provided under NRC contract.

Within the DOE, there is a move towards the use of technical standards in place of separate DOE Orders. Mr. Robert Oldham attended N-15 committee meetings at the Institute for Nuclear Materials Management (INMM) annual conference to obtain further information on the use of technical standards in place of DOE Orders. The Office of Safeguards and Security asked NBL for a writing chairperson for a new proposed American National Standards Institute (ANSI) standard on material protection, control and accountability (MPCA) systems. The language of the standard should meet the needs of varied nuclear facilities including domestic DOE facilities, NRC licensed facilities and international nuclear facilities. NBL personnel also participated on INMM/ANSI 5.2 sub-committee on Mass Measurements Control, ANSI/INMM N-15-5.5 Volumetric Measurement Control Committee, American Society for Testing and Materials (ASTM)/C26.05 Nuclear Fuel Cycle-Methods of Test subcommittee, and International Organization for Standardization (ISO)/Technical Committee 85/Standards Committee 5/Working Group 1.

NBL Support to the Central Training Academy

NBL personnel provided assistance to CTA with preparation and presentation of CTA MC&A course lectures for MCA 140, "Basics of MC&A Measurements," MCA 144, "Measurement Control Programs in Material Control & Accountability," MCA 132, "Sampling Plans for Material Control and Accountability," and MCA 142, "Volume Measurement Techniques." NBL personnel continued working with the Central Training Academy in the development of a new correspondence course, CTA MCA 104-D, which will be a prerequisite for both the MCA 140 and MCA 144 courses. Personnel supporting the Central Training Academy coursework are Dr. Kenneth Lewis, Mr. Robert Oldham, Mr. Michael Soriano and Ms. Margaret Legel.

Site-Specific Assistance

At the request of the Operations Offices, NBL assists sites in meeting analysis needs to improve the safeguards measurement posture of the site. Extensive laboratory effort was expended in FY 94 in the analysis of uranium-aluminum ingots to assure that a consensus NDA reference material is available to both Savannah River Site (SRS) and the Oak Ridge Y-12 Plant to avoid shipper/receiver differences. Mr. Robert Oldham attended concluding meetings held at both SRS and at the Y-12 Plant to discuss the analytical characterization results obtained by all facilities. The NDA reference materials at SRS and Y-12 will be calibrated using standard values based on grab melt sampling and SRS/NBL chemical analysis. NBL

also offered assistance to the Oak Ridge Y-12 Plant for method qualification for a uranium isotope dilution measurement procedure which will replace a method that currently generates mixed waste.

International Safeguards Assistance

NBL personnel continued to support International Safeguards projects through NN-40, NN-44, NN-50, and NE-33 for Russia, Ukraine, Kazakstan, Uzbekistan, and for ABACC. Seven NBL personnel travelled internationally in support of these projects to Russia, Kazakstan, Uzbekistan, Ukraine, Argentina and Brazil. Two NBL personnel completed Russian High Enriched Uranium Transparency Monitor training. A separate report in this Progress Report provides details of these activities.

INTERNATIONAL SAFEGUARDS ASSISTANCE

W. G. Mitchell, M. A. Legel, H. R. Martin, K. Lewis, C. D. Bingham,
M. W. Thomas, D. T. Baran, M. I. Spaletto, and R. D. Oldham

Summary of FY 95 Assistance for International Safeguards

During FY 95 NBL provided assistance to NN-1 and to the Office of Uranium Programs (NE-30) for international activities. The assistance included work in Material Protection, Control, and Accounting (MPCA) for FSU Task Force in the International Safeguards Division (NN-44); Office of Arms Control and Nonproliferation (NN-40); and the Office of Security Affairs (NN-50). In FY 95 NBL personnel interacted as part of DOE delegations or U. S. government interagency review teams with the Russian Federation; the FSU states of the Ukraine, the Republic of Kazakstan, and Uzbekistan; and ABACC. NBL's role on these projects was to provide expert MC&A reviews, and in some cases, to recommend equipment needs to Department of Defense. In addition, NBL personnel participated in an initial monitoring trip, training for DOE monitoring teams, document preparation, and evaluations/discussions for proposed blind sample exchange programs for the High Enriched Uranium (HEU) blend-down program with Russia under the auspices of the Office of Uranium Programs/Facility and Technology Management Division (NE-33).

Russian Federation

Dr. H. Rodney Martin travelled with a U.S. delegation in October 1994 to provide Safeguards expertise for the U.S. bilateral review of Russia's Mayak site. Other activities included procurement of seals as part of the equipment to be supplied to Mayak. Specific recommendations included the utilization of better seals, implementation of inventory confirmation checks, and upgrades to physical security equipment to increase delay times and to improve detection mechanisms.

Ukraine

Dr. Carleton Bingham participated in follow-up meetings and discussions from an August/September 1994 visit to the Ukraine Nuclear Power Plant (SUNPP) and the Kiev Institute for Nuclear Research (KINR). Team members prepared lists and specifications for equipment to support KINR and SUNPP. Dr. Bingham was responsible for collating the MC&A team members report for the final survey report.

Kazakstan

Dr. Wanda Mitchell participated on a review team to facilities in the Republic of Kazakstan in September-October 1994. The purpose of the trip was to provide expert MC&A and physical protection reviews of Kazakstan's nuclear facilities and to recommend equipment needs to the U.S. Department of Defense. The facilities visited were the Ulba Fuel Fabrication Facility in Ust-Komenogorsk and the Research Reactors at Semipalatinsk-21. At the Ulba Fuel Fabrication Facility, training and equipment needs were identified. Additional assistance requested was for a visit to a U.S. fuel fabrication facility during inventory and information on material balance structures. At the Semipalatinsk-21 facility, which consists of three research reactors and storage facilities, training and equipment needs were identified. Additional assistance for calculations for reactor inventories was also identified. Dr. Mitchell was responsible for collating the MC&A team members report for the final survey report.

Dr. Wanda Mitchell attended a briefing at the State Department in Washington D.C. on the status of fulfilling the equipment part of the Sapphire agreement (enriched uranium purchase) with Kazakstan. The Team met again in March 1995 in Kazakstan with U.S. Embassy personnel and the Minister of Science of the Republic of Kazakstan in Almaty and with Ulba facility personnel in Ust Kamenogorsk on the project preparations identified as the means of providing equipment to Kazakstan facilities. Instrument specifications and sole source justifications for equipment were prepared for the Ulba Plant for an additional $3 million in Nunn-Lugar funding.

Dr. Wanda Mitchell made a third trip to Kazakstan for a review at the BN-350 reactor in Aktau and the VVR-K research reactor in Almaty in August-September 1995. Preparation of a Program Plan for these facilities has begun.

Uzbekistan

Mr. Martin Thomas travelled to Uzbekistan with a team from NN-44 in June 1995 to provide expert safeguards and security (S&S) reviews of Uzbekistan nuclear facilities and to identify S&S systems upgrade

needs. As a participant in a second trip in September 1995, he briefed the host country regarding the applicable IAEA Information Circular (INFCIRC) requirements and the assessments and recommendations resulting from the June assistance visit; courses of action were recommended for facility upgrades.

ABACC Assistance

Mr. Robert Oldham and Ms. M. Irene Spaletto reviewed the ABACC network laboratory facilities including CNEA Headquarters; the Atomic Center Constituents; and the Ezeiza Atomic Center (Buenos Aires, Argentina); IPEN (Sao Paulo, Brazil); CDTN (Belo Horizonte, Brazil); and LASAL (Rio de Janeiro, Brazil) in November 1994. ABACC Headquarters in Rio de Janeiro, Brazil was also on the agenda. The visit served as a reciprocal information gathering visit to that of ABACC personnel to NBL in FY 94. ABACC, a bilateral organization with oversight for safeguarding nuclear reactor materials in Argentina and Brazil, is in the process of developing oversight capabilities and sought information from NBL regarding accountability measurements, measurement control, and measurement exchange programs. Additional areas of future cooperation between ABACC and NBL were identified and proposals were drafted and submitted to NN-44 for funding consideration. The proposals were discussed at the Permanent Coordinating Group meeting in September 1995 with some accepted for FY 96 funding. The New Brunswick Laboratory completed analytical measurements to meet commitments under Action Sheet 3 of the ABACC agreement.

HEU Blend Down Monitors

The Department of Energy began training U.S. monitors of the blend-down of highly enriched uranium extracted from Russian nuclear weapons (HEU Transparency agreement) with subsequent shipment of the low enriched uranium to the Portsmouth Gaseous Diffusion Plant. Because NBL personnel have MC&A expertise and are federal employees, NE-30 requested that four be identified to participate and perhaps lead these monitoring teams.

Dr. David Baran and Ms. Margaret Legel completed the Russian Transparency Monitor Training in October 1994. NBL personnel worked on the drafting of Annex 14 to the Transparency Agreement Between the Government of the United States of America and the Government of the Russian Federation on the oversight of the Russian blending of uranium. Dr. Kenneth Lewis attended an April 1995 meeting at Lawrence Livermore National Laboratory (LLNL) to review and concur on the Health and Safety Plan for the HEU Transparency Implementation. Dr. Baran travelled to LLNL to evaluate NDA instrumentation for the Monitoring Program and to Yekaterinburg, Russia in April 1995 in support of the Monitoring Program.

Dr. H. Rodney Martin and Dr. Kenneth Lewis attended meetings and discussed proposed blind sampling programs for the Yekaterinburg Ural Electrochemical Integrated Plant (UEIP) at a meeting held at the Portsmouth Gaseous Diffusion Plant as well as during follow-up conference calls. Trips to Yekaterinburg for Dr. Lewis were scheduled, then postponed until FY 96.

REFERENCE MATERIALS PROGRAM

C. G. Gradle

Program Administration

NBL, as the U. S. government's nuclear reference materials laboratory, continued providing CRMs to meet the needs of the Nuclear Safeguards Community. These CRMs provide assurance that safeguards measurements meet essential compatibility, reliability and traceability to the national measurement base. During this fiscal year, program activities included increased CRM sales and better customer service; preparation and certification of new and replacement CRMs; planning for new CRMs that will meet the needs of the nuclear safeguards community; and providing support to various safeguards-related functions.

In FY 95, 461 units of 41 different CRM's were sold for a total cost of $133,691.50. A detailed discussion of sales and shipping issues is presented in a separate report in this Progress Report.

In order to replenish the low inventory at the laboratory of CRM 116, uranium metal, the bulk material was shipped from Lockheed Idaho and packaged into 257 units. Savannah River Facility provided the Chalfant containers used to ship the material. The remaining inventory is still at Lockheed Idaho. Enriched uranium reference material bulk metal and oxide currently in storage at the Idaho Chemical Processing Plant (ICPP) has to be moved before ICPP is transferred to EM Programs. MC&A personnel at Y-12 have indicated their willingness to receive these materials for retrievable storage. Actual transfer of material may be delayed until the next fiscal year due to the shut-down of the Y-12 plant and transportation issues that needs to be addressed.

Certification Projects

NBL continued to prepare uranium and plutonium "blind standards" for different measurement methods to meet its own internal measurement quality control requirements. This fiscal year over 800 blind standards were prepared and distributed.

The replacement of several NBL uranium isotopic reference materials is being made using smaller quantities in ready-to-use ampulated solutions. Providing these materials in the form of a uranyl nitrate solution in dilute nitric acid media will allow customers to load directly from the CRM unit as purchased and minimize the risk for contamination. Projects are in progress to certify the following uranium isotopic NBL CRMs: U0002-A, U007, U010-A, U015-A, U050-A, and U930-D. The status of U930-D and U010-A projects are presented in separate reports in this Progress Report.

The recertification of a set of four NBL CRM 42(1-4), uranium counting standards is in progress. The uranium concentration of this series range from 0.5% to 4%. Bulk material for each CRM was blended and packaged into 250 units. Preliminary tests on density and homogeneity were completed; certification work is in progress. Because this is a recertification effort, the material will be designated as CRM 42A(1-4). A discussion of this project is presented in a separate report in this Progress Report.

NBL obtained additional funding outside of the Office of Safeguards and Security in support of Certified Reference Materials useful in DOE and NRC Programs. The Oak Ridge Y-12 site and ANL-W contacted NBL regarding preparation of site-specific nondestructive assay reference materials. The Y-12 proposal was accepted and funded by Y-12 through March 1996. NBL is preparing three sets of uranium concentration and isotopic standards, for use in calibration of nondestructive gamma-ray spectroscopy instrumentation. These standards are doubly contained in low atomic weight material for use with site specific matrix. A discussion of this project is presented in a separate report in this Progress Report.

Funding obtained from NRC enabled the replacement of CRM 125-A, a uranium pellet standard. As a joint effort between DOE and NRC, Westinghouse Commercial Nuclear Fuel Division provided NBL with the base material, and NBL packaged and certified the uranium oxide pellet standard. Costing for over 3900 units packaged was completed and a large number of these units were purchased by NRC. A discussion of this project with the Certificate of Analysis for this standard is presented in a separate report in this Progress Report.

DOE/EM-334 funding was obtained for the preparation of a uranyl nitrate reference material, CRM 145, for qualification of NBL low-level uranium instrumentation and for sale to additional customers. NBL prepared and certified 500 units of CRM 145. Costing and preparation of the certificate will be completed during the next fiscal year. A discussion of this project is presented in a separate report in this Progress Report.

Domestic Activities

Support was provided to Westinghouse Hanford for shipment of excess PuO_2 inspection samples to IAEA. Copies of certificates of competent authority, past and present, for the SAFPAK container and a copy of the NBL report on operational testing of the PAT-2 container were shipped to the facility. This information was then followed-up with shipment of two SAFPAK containers, three PAT-2 containers, and a SAFPAK leak tester to the facility in early November, 1994.

NBL provided EG&G's Special Technologies Laboratory (STL) with quantities of low- and high-enriched uranium materials for NDA measurement during an interagency exercise in July, 1995. The low-enriched material can also be used to establish traceability to the NBL measurement base by STL if neutron NDA methods are developed there.

NBL participated in a joint project with two U.S. Laboratories. NBL received PuO_2 samples from Los Alamos National Laboratory for performing verification measurements for a calorimetry standard. Additional measurements will be performed at both Los Alamos National Laboratory and Westinghouse Hanford before a reference value is assigned to the plutonium used to prepare the calorimetry standard.

An investigation into the replacement for an out-of-stock UF_6 uranium assay reference material (CRM 113) is being made. This may be possible through cooperation with the Portsmouth Gaseous Diffusion Plant, providing packaging, prior to NBL's making certification measurements.

International Activities

In response to a request from IRMM (Geel, Belgium), detailed information on CRMs 101-A through 105-A base silica material, uranium impurities in the silica material, and reference material homogeneity was provided. NBL also shipped small samples of CRMs 105-A and 108-A, Monazite Sand, to IRMM for particle analysis. IRMM is testing the feasibility of these materials for distribution within the REIMEP.

Discussions on NBL support to the IAEA-proposed activities for safeguards environmental-level reference materials were consolidated into a proposal. This will be a joint project with U.S. laboratories and the IRMM with oversight by the IAEA. The project involves certifying and providing a series of uranium and plutonium environmental-level reference materials. The project work at NBL will begin early next fiscal year with funding provided by International Safeguards Project Office/Brookhaven National Laboratory (ISPO).

Discussion were held with IAEA personnel on the Pu-244, CRM 131 replacement standard. This will be U.S., European, and Russian joint project work. NBL is also considering projects to serve the reference materials needs of DOE activities associated with the Former Soviet Union.

ASTM/ANSI Activities

NBL personnel attended various meetings to provide support to safeguards related committees and programs. Support was provided to ASTM C-26, the uranium and plutonium task groups, in the area of plutonium mass spectrometric and uranium dissolution methods. Standards were reviewed and changes were submitted to ASTM headquarters for ballot. NBL presented information on the OSS/NBL Guide on traceability for NDA working reference materials to the NDA subcommittee. Support was provided to ANSI/INMM N15-5.2 and N15-5.5, the Mass Measurement and Volumetric Measurement Control Committees.

REFERENCE MATERIAL SALES

C. G. Gradle and J. B. Jeans

NBL as the U. S. government's nuclear reference materials laboratory, continued sales of CRMs to meet the needs of the nuclear safeguards community. Transportation issues and certification of shipping containers were pursued in an effort to provide timely service. During this fiscal year, upgrades to CRM data files were accomplished to help provide better customer service.

In FY 95, 54 different CRM's were available for sale. Of these, 41 CRMs had sales ranging from 1 to 163 units. A listing of FY 95 sales of ten or more CRM units is provided in Table I. Purchasers of CRMs represented 54 separate organizations, including 8 U.S. DOE contractors, 18 U.S. NRC licensees, 3 U.S. academic institutions, 1 other U.S. customer and 24 facilities in 14 foreign countries. A total of 91 orders (31 foreign and 60 domestic) for 459 units (319 foreign and 140 domestic) valued at $133,691.50 were shipped. Special standards for the Oak Ridge Y-12 site valued at $95,401.00 were fabricated at NBL to meet the site's uranium non-destructive assay measurement needs. Figure 1 shows market shares of sales for FY 95 and each of the prior four years.

A re-costing of historical reference materials was completed to reflect current costs for order handling. An agreement was made to allow for annual inflation adjustment of each individual reference material price from the date of certification to 1995. A revised Price List was issued and transmitted to customers on the mailing list.

The CRM catalog, Material Safety Data Sheets, and most certificates of Analysis were formatted in wordperfect and made available on the NBL local area network. Changes and updates may be made on a real-time basis. Printing of these materials and binding of the catalog are done in-house as needed to minimize waste.

There were no significant changes to the nuclear materials shipping situation. For foreign shipment of Type B radioactive materials, certification of the Croft Associates SAFPAK (2767) and SAFKEG (2799) shipping containers was continued. However, approval for domestic use of these containers for Type B shipments of radioactive materials continues to be a problem. The limited availability of approved Chalfant containers (approximately 50 throughout the DOE complex; only 11 of these have double liners which allow oxide or solution shipment) exacerbates this problem. The shipping constraints in turn impede the sales and certification efforts of several CRMs.

NBL pursued discussions with the NN-40 personnel who have primary interest in the approval process for foreign orders. At the end of this fiscal year, NBL is waiting for approval for shipment of a foreign order to ABACC.

TABLE I

FY 95 SALES BY CRM

			UNITS SOLD		
RANK	CRM #	DESCRIPTION	FOREIGN	DOMESTIC	TOTAL
1	116	ENRICHED U METAL	161	2	163
2	129	U_3O_8 ASSAY	18	24	42
3	108-A	MONAZITE-SILICA	3	20	23
4	130	^{242}Pu SPIKE	10	12	22
5	U050	U ISOTOPIC, 50%	18	0	18
5	109-A	MONAZITE-SILICA	6	12	18
6	U005-A	U ISOTOPIC, 0.5%	17	0	17
7	124(1-7)	U_3O_8 IMPURITIES	13	3	16
8	115	DEPLETED U METAL	0	14	14
9	111-A	^{233}U SPIKE	12	0	12
10	106-A	MONAZITE-SILICA	1	10	11

PREPARATION OF NON-DESTRUCTIVE ASSAY GAMMA-RAY SPECTROSCOPY REFERENCE STANDARDS: STATUS REPORT

J. P. Zebrowski, D. T. Baran, G. A. Sowell, K. D. Johnson, A. J. Traina, and M. M. Smith

NBL functions as the U.S. certifying authority for nuclear reference materials and also provides site-specific safeguards assistance to DOE facilities. The waste management division of the Lockheed Martin Y-12 Plant has requested that NBL prepare standards, traceable to the national measurement base for both uranium assay and isotopic composition, for use in calibration of nondestructive assay gamma-ray spectroscopy instrumentation. Y-12 Plant has requested three sets of standards:

1) standards prepared from CRM U005-A (nominally 0.5% ^{235}U) containing varying quantities of uranium ranging from 0.1 g to approximately 7.5 g U,
2) standards prepared from CRM U930 (nominally 93% ^{235}U) containing eleven different quantities of uranium ranging from 1.0 mg to 20 mg U, and
3) a group of standards containing 1 g U prepared from CRMs with the following nominal ^{235}U enrichments: 0.02% 0.5%, 1.5%, 3%, 5%, 10%, 35%, 50%, 75%, 85% 90%, and 93%.

As part of this project, NBL has had to develop an appropriate preparation and packaging method for these standards. Self-absorption of the uranium gamma-ray emissions must be minimized in the standards in order to ensure a valid calibration of the NDA instrumentation. Additionally, the Y-12 site, for safety reasons, has a requirement that the nuclear material be doubly contained. Both the primary and secondary containers must be made from low atomic weight materials to minimize gamma-ray attenuation by the packaging. Since self-absorption of gamma-ray emissions increases as the uranium becomes more densely packed, a diffuse geometry for the uranium is necessary. The design that was ultimately accepted has the uranium encased in a thin laminate and placed on the inside of a leakproof tube or bottle (thus providing dual containment). This design essentially fixes the uranium in shape of a cylinder, leading to low uranium density and, therefore, low self-absorption.

In order to achieve a cylindrical geometry, the uranium initially has to be fixed onto a thin, flexible substrate. The substrate used is similar to filter paper and is composed of a borosilicate fiber woven into sheets, with a polyester backing to increase its strength. As an additional precaution, a thin layer of polyester with an adhesive backing is attached to the substrate. This gives added assurance that the uranium, which is added onto the substrate as a solution, remains within the substrate.

NBL isotopic CRMs will be used as the source of uranium in the NDA standards. These uranium oxide powders will be dissolved in a minimal amount of nitric acid, the solutions will be brought to dryness to remove excess nitric acid and will be then redissolved in an appropriate amount of water. Isotopic verification measurements will be performed on the solutions. Additionally, chemical analysis for certification of elemental uranium content will be performed. Actual traceability comes from standards used with titrations plus traceable weights for aliquanting. The solution will then be weight aliquanted onto the substrate. This process gives a reasonably uniform distribution of the uranium on the substrate. The borosilicate fibers in the substrate act to hold the uranium within the weave.

After air drying, a spray enamel is used to fix the uranium onto the substrate. The substrate is then folded over, placed between two sheets of plastic, and the plastic sheets are laminated together. This constitutes the primary container. The plastic laminate is composed of polypropylene on the inside (the uranium containing side) and a polyester coating on the outside. The laminated substrate is rolled into the secondary container such that the uranium-containing paper essentially forms a cylinder around the inside of the secondary container. The secondary containers vary in size, ranging from 10-mL Teflon® FEP Oak Ridge centrifuge tubes to 500-mL Nalgene® polyethylene bottles.

The resulting standards, in addition to having low attenuation of the gamma-ray emissions, are also small and rugged enough that they can readily be placed into any simulated matrix to allow for adequate compensation of matrix effects. The same standards can be used for radically different matrices.

Overall, the design of the standards lends itself to great flexibility. The mass sizes of the standards and the isotopic composition of the uranium could be altered to meet a particular site's needs and instrumental sensitivity. Uranium isotopic contents could range between 0.02% and 97% ^{235}U. These are the currently certified uranium isotopic suite. If a site uses NDA as a way to quantify total uranium by looking at the ^{235}U gamma-ray peak, when ^{235}U enrichment is known from process knowledge, then standards could be made using highly enriched uranium as a source even if the typical samples contain only low enriched material. This method would allow, effectively, high mass standards in a compact size container.

Design and testing of the containment was completed in FY 95. Tests show high transmission in the laminated substrates ranging between 94-99% which gives correction factors of 1.04 or less. This correction factor does not account for the attenuation due to the secondary container, though that should be minimal. Production of the first set of standards has begun, and all standards are expected to be completed by the end of the second quarter of FY 96.

PREPARATION AND CERTIFICATION OF CRM U930-D: STATUS REPORT

P. M. Santoliquido, P. V. Croatto, F. E. Jones, A. J. Traina, I. W. Frank, and M. M. Smith

NBL provides a suite of certified uranium isotopic reference materials which span enrichment levels from depleted to highly enriched. Each unit consists of a nominal one gram of uranium in the form of a highly-purified U_3O_8 powder. The supply of one of these CRMs, CRM U930 (nominally 93% ^{235}U), has become exhausted. A replacement bulk material pulled from storage exhibited differences in minor isotope content from that specified on the certificate of analysis for the original CRM. Consequently, NBL has initiated a certification of the material as a new CRM, CRM U930-D.

A decision was made to replace the solid oxide form with a uranyl nitrate solution that has a nominal concentration of 1 mg U/g solution. This change has several advantages. The original unit of one gram of uranium provided an amount of uranium in great excess of what was needed for routine isotopic analysis. A single unit would thus remain in use for a long period of time, necessitating multiple subsampling, creating a risk of cross-contamination. The smaller unit provides a more appropriate quantity of uranium, resulting in less waste production. Finally, the liquid form in the prepared concentration provides a ready-to-run preparation for thermal ionization mass spectrometry.

The first step in the preparation of the new CRM was to blend the bulk material in a Turbula® Mixer. A portion of the blended material was then ignited to constant weight at 800°C, weighed, dissolved and made up to a nominal concentration of 1 mg U/g solution. An automated ampulator-sealer was used to package the CRM solution into 5 mL ampules with break-off tips for ease of use.

Following a statistical plan designed by the NBL Numerical Analysis Group, two analysts performed a full isotopic analysis by thermal ionization mass spectrometry using two Finnigan-MAT 261 instruments equipped with 13-sample turrets. After ampulation, ten ampules were selected for mass spectrometry, following a statistically-designed sampling plan. Of these, five ampules were assigned to each mass spectroscopist. Each mass spectroscopist analyzed two samples from each of the five assigned ampules and one sample from each ampule assigned to the other mass spectroscopist. The mass discrimination factor was determined using NBL CRM U500; CRM U930 was utilized for quality control. Each turret included three CRM U500 aliquants, five CRM U930 aliquants, and five CRM U930-D aliquants.

Statistical evaluation of the data is in progress; certification will be completed in FY 96.

PREPARATION AND CERTIFICATION OF CRM U010-A: STATUS REPORT

P. M. Santoliquido, P. V. Croatto, A. J. Traina, F. E. Jones, I. W. Frank, and M. M. Smith

NBL provides a suite of certified uranium isotopic reference materials which span enrichment levels from depleted to highly enriched. Each unit consists of a nominal one gram of uranium in the form of a highly-purified U_3O_8 powder. One of these CRMs, CRM U010 (nominally 1% ^{235}U), is in short supply. NBL has initiated replacement of this material on a high priority basis, as this material is in high demand because its isotopic composition is the closest among the available CRMs to natural uranium.

A decision was made to replace the solid oxide form with a uranyl nitrate solution that has a nominal concentration of 1 mg U/g solution. This change has several advantages. The original unit of one gram of uranium provided an amount of uranium in great excess of what was needed for routine isotopic analysis. A single unit would thus remain in use for a long period of time, necessitating multiple subsampling, creating a risk of cross-contamination. The smaller unit provides a more appropriate quantity of uranium, resulting in less waste production. Finally, the liquid form in the prepared concentration provides a ready-to-run preparation for thermal ionization mass spectrometry.

Since the bulk oxide from which the original CRM U010 was made is no longer available, the new CRM U010-A was prepared in-house by blending currently available isotopic materials. CRM U0002 (nominally 0.02% ^{235}U) and CRM U850 (nominally 85% ^{235}U) were chosen to be blended in order to produce minor isotopic ratios representative of true process material of this enrichment. Sufficient quantities of both CRM U0002 and CRM U850 were separately ignited to constant weight at 800°C before being weighed out. The required amount of CRM U0002 was dissolved, and then reduced to near-dryness.

For the batch size prepared, the amount of CRM U850 required was very small. Therefore, in order to minimize the impact of weighing error, an amount twenty times the target amount was weighed out, dissolved and diluted to 100 mL of solution. A 5 mL aliquant of this solution was added to the CRM U0002 to achieve a ^{235}U composition of 1%, and the combined materials diluted to a nominal concentration of 1 mg total U/g solution. An automated ampulator-sealer was used to package the CRM solution into 5 mL ampules with break-off tips for ease of use.

Certification of this new material will be completed in FY 96.

REPACKAGING OF CRM 42(1-4) COUNTING STANDARD MATERIALS

K. S. Scheidelman, P. V. Croatto, P. B. Mason, G. A. Sowell, A. V. Stiffin, I. W. Frank, G. J. Orlowicz, M. M. Smith, A. J. Traina, F. E. Jones, D. E. Dallmann, and A. M. Voeks

To replenish the low inventory of CRM 42(1-4), a set of four uranium counting standards, the original bulk materials were retrieved from storage and repackaged into individual units. The bulk materials for these standards were originally prepared from pitchblende diluted with dunite. The dunite diluent is a dense igneous silicate of magnesium and iron. The uranium concentrations of the four levels of this set of standards range from 0.5% to 4%; the standards are used for calibrating counting equipment.

The bulk material for each level was sampled and subjected to preliminary analysis. The material density, percent moisture loss on drying at 110°C, and determined uranium concentration indicated no loss of material integrity. The bulk material was then processed and tested for homogeneity: the material was passed through a 30-micron mesh sifter and then blended in a large stainless steel V-blender. Grab samples were taken from the blender to test for homogeneity of the blended material. These grab samples were dissolved, and aliquants from each dissolution were analyzed for uranium by the Low-Level NBL-modified Davies and Gray Titrimetric Method. Results of the analyses for uranium concentration from this homogeneity testing study are shown in Table I and compared to uranium concentrations obtained from previous certification measurements. Acceptance criterion was agreement of equal to or better precision than the original certification results for all grab samples within each level. The results of uranium concentration expressed as percent uranium (%U) with its relative standard deviation (%RSD) agreed well with the original certification data, indicating that the blending was satisfactory. The blended bulk material was then packaged into 240 units for each level with a nominal weight of 100 grams per unit. These standards will be recertified because the original certification was done more than 30 years ago.

TABLE I

RESULTS AND COMPARISON OF HOMOGENEITY TESTS FOR CRM 42(1-4)

Laboratory (Year)	NBL (1957)			NBL (1995)		
Material	n	%U	%RSD	n	%U	%RSD
CRM 42-1	9	4.03	0.87	6	4.00	0.41
CRM 42-2	10	1.99	0.45	6	1.95	0.34
CRM 42-3	10	1.07	0.39	4	1.03	0.30
CRM 42-4	10	0.52	1.54	4	0.48	0.98

PREPARATION AND CERTIFICATION OF CRM 145, URANYL NITRATE SOLUTION

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A. J. Traina, M. D. Soriano, F. J. Orlowicz, and D. E. Dallmann

Introduction

NBL received $60,000 in EM-334 funding for the preparation and certification of a uranyl nitrate solution reference material. This certified reference material, CRM 145, will provide a convenient and easy-to-use source of uranium for preparation of standards for quality control, instrument calibration, and other purposes. Additionally, a portion of this material will be diluted, and the new lower-level solution certified at a later date. CRM 145 and the lower-level solution will both be used for the qualification and intercomparison of such NBL instrumentation as a laser kinetic phosphorescence analyzer, x-ray fluorometer, inductively coupled plasma-optical emission spectrometer and inductively coupled plasma-mass spectrometer. These instruments will provide NBL with the ability to perform environmental-level measurements of in-house and outside samples.

Preparation and Certification

Approximately 106 grams of NBL CRM 112-A, Uranium Metal Assay Standard, were cut, the oxide coating removed with acid, and the cleaned metal weighed and dissolved in nitric acid. The resultant solution was further diluted with nitric acid and distilled, deionized water to create ten liters of a 1 molar nitric acid solution containing approximately 10 mg U/gram solution. A Cozzoli automatic ampulator was used to aliquant and seal this solution into washed glass ampules, resulting in nearly 500 ampules each containing approximately 20 mL of solution. Twenty ampules were removed at intervals from the production line according to a statistical plan. Each of these ampules was decanted into a polyethylene bottle, with five samples then aliquanted from each bottle for uranium analysis by the NBL-modified Davies and Gray titration. Additionally, two samples from each of three ampules were aliquanted for analysis by thermal ionization mass spectrometry in order to confirm the isotopic composition and atomic weight of the uranium.

Of the five aliquants from each of the twenty ampules to be subjected to the NBL-modified Davies and Gray titration, four were analyzed with the fifth held in reserve as a spare. Two analysts performed the titrations, each analyzing two aliquants from each of the twenty ampules. The titrations were performed over four days, with 10 samples and 4 quality control "blind" samples (QC blinds) analyzed each day. The results were then subjected to statistical analysis. Three samples and two QC blinds were found to be statistical outliers and were removed from the data analysis. No statistically significant analyst-to-analyst or bottle-to-

bottle variation was found. Each analyst exhibited significant day-to-day variation both in the samples and the QC blinds. When the sample data were corrected for the daily QC blind means, the statistically significant day-to-day variation was eliminated. The final results of the QC blind-corrected sample data, including propagated uncertainty of the QC corrections, are as follows:

QC-corrected Mean (mg U/g sample):	10.13146
Standard Deviation:	0.000355
95% Confidence Interval:	±0.00074
95% Confidence Interval (percent):	±0.0073%

Results of the thermal ionization mass spectrometric analysis were consistent with normal uranium and indicated no anomalies. Following data analysis, the remaining ampules were labeled and stored subsequent to issuance of a certificate of analysis.

Conclusion

From EM-334 funding, NBL prepared and certified 500 units of CRM 145. This CRM is a uranyl nitrate solution, with each unit containing 20 mL of solution of 10.13 grams of uranium per gram of solution concentration. The CRM is intended to serve as a source of uranium for quality control and instrument calibration. It will also serve as a base material for a lower-level solution suitable to serve the same purposes for environmental measurements.

CERTIFICATION OF CRM 125-A, URANIUM DIOXIDE PELLET

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K. S. Scheidelman, I. W. Frank, A. V. Stiffin, and M. D. Soriano

As a collaborative effort between the DOE and the NRC, the NBL has packaged and certified a uranium dioxide pellet standard as CRM 125-A. Westinghouse Commercial Nuclear Fuel Division, an NRC licensee, supplied NBL with the base material of which the CRM is composed, a single production batch of UO_2 pellets. These pellets were sintered at 1700°C for 20 hours in a reducing atmosphere; this produces a ceramic-like material that is resistant to moisture uptake and stable when exposed to air.

After arrival at NBL, the pellets were packaged individually in glass vials with snap caps. A piece of low-lint tissue was used for padding, to prevent chipping of the pellet.

Twenty pellets were randomly selected from the packaged units for analysis of both uranium elemental composition and isotopic distribution. The pellets were dissolved in a mix of 8 *M* HNO_3 and HF, and

duplicate aliquants were taken for analysis by both mass spectrometry and high-precision titration. After appropriate sample preparation and redissolution, all aliquants were analyzed following a statistically-designed plan.

Isotopic measurements were performed by a single analyst utilizing a Finnigan-MAT 261 thermal ionization mass spectrometer with a 13-sample turret. The mass discrimination factor was determined utilizing NBL CRM U500; CRMs U030 and U050 were utilized for quality control. Each turret included a minimum of four quality control standards, including at least one CRM U500. Each sample's duplicates were placed in random fashion on the same turret, confounding pellet-to-pellet with turret-to-turret variation. Statistical analysis identified one standard run and two sample runs as outlying; these were excluded from further statistical analysis. In the quality control runs, no statistically significant turret-to-turret (or pellet-to-pellet) variation was found; on the sample runs, however, statistically significant turret-to-turret variation was found in both the ^{235}U and ^{238}U results. This variation, which was small compared to the within-turret variation, was propagated together with the within-turret variation to produce the final 95% confidence intervals (C.I.) for the mean values of each of the isotopic abundances expressed in atom percent.

Uranium elemental composition measurements were performed by two analysts utilizing the NBL high precision titration. Each analyst analyzed ten pellets in duplicate over five titration days. Aliquants of a solution of NBL CRM 112-A, Uranium Metal Assay Standard, were used for quality control. Each analysis day, 3 quality control standards and 4 sample aliquants were titrated. As with the isotopic measurements, each sample's duplicates were analyzed on the same day. One standard analysis and five sample analyses were identified as outlying; these results were excluded from further statistical analysis. Statistically significant pellet-to-pellet variation was found in the titration results of one analyst but not in the results of the other analyst. In order to determine if the variation was due to pellet inhomogeneity or due to variations introduced by the preparation of the materials for titration, eight pellets were analyzed by gravimetry. Only the standard deviation of the results was considered; this very small number (0.0026%) indicated that the pellet-to-pellet variation was negligible compared to the precision of the titrimetric method and can be ignored. The simple mean of the analysts' results was used as the certified value; the individual 95% confidence intervals were pooled to produce a combined 95% C. I. for the mean value. All certified values are displayed on the following certificate.

Since the NRC supplied a large portion of the funding for the certification effort, a supply of the CRM will be set aside for NRC fuel fabricators. The pellets will also be used as a test material for selected NRC licensees in the Safeguards Measurement Evaluation Program, and will also be available for sale.

SAFEGUARDS MEASUREMENT EVALUATION PROGRAM

M. I. Spaletto, M. M. Smith, M. D. Soriano, and M. E. Downey

SME Program Information

The NBL provides technical support to the DOE/OSS by independently evaluating the adequacy of measurement programs as applied to materials accounting in DOE nuclear facilities. This support is provided through operation of the NBL SME Program, which monitors the quality of uranium elemental concentration and uranium and plutonium isotopic abundance destructive analyses.

The NBL SME Program was developed as a means to monitor and evaluate the quality and effectiveness of nuclear material measurements by site, Material Balance Area (MBA), or unit process. The Program's goal is accomplished through the selection of site-specific evaluation materials, which are prepared, characterized, and distributed to participating facilities for analysis. Reported measurement data are statistically evaluated, and reports are issued to the contractor, the cognizant DOE Operations Office, and DOE Headquarters. Utilizing information included in the DOE/OSS Measurement Control Guide and Measurement Improvement Plan, SME Program reports include an evaluation as to whether or not the reporting facilities have achieved accuracy and precision within appropriate target values.

Accomplishments for FY 95 include development of a database application for the statistical evaluation of submitted results, to replace an outdated system. This new application streamlines the entire process of statistical evaluation, from data entry to report and graphics generation.

A cooperative agreement was reached between DOE/OSS/NBL and the NRC to include selected NRC fuel fabrication licensees in the Program; full participation by the NRC licensees will begin next fiscal year.

Normal Uranyl Nitrate Material

Normal uranyl nitrate solutions enable the participation of facilities restricted from receiving shipments of enriched materials. A suite of three solutions is distributed to participants through the Program. The elemental assay of each solution differs from the next by approximately 0.15 to 0.2%; the ability to differentiate these materials demonstrates good analytical capabilities.

Los Alamos National Laboratory (LANL), Paducah Gaseous Diffusion Plant (GDP), Portsmouth GDP, NBL, and the Y-12 Plant are participating in the normal uranyl nitrate portion of the Program to evaluate uranium

assay accountability measurements on solution samples at their respective facilities. Twenty-eight final reports were issued to the facilities and cognizant Operations Offices through September, 1995. Analyst-to-analyst differences observed in the submitted data assisted in evaluating analyst training; observed day-to-day differences assisted in identifying instrument problems. These materials serve to demonstrate acceptable laboratory performance for accountability measurements.

Enriched Uranyl Nitrate Material

The Program also has available for distribution three high-enriched (approximately 90% ^{235}U) uranyl nitrate solutions, a solution of 50% enriched uranyl nitrate, and a 4% low-enriched solution for isotopic analysis. All solutions, except for the 4% enriched solution, are also characterized for elemental concentration, enabling them to be used in isotope dilution mass spectrometry (IDMS).

Argonne National Laboratory - West, NBL, Savannah River Plant, and the Y-12 Plant submitted results from isotopic analyses of the enriched uranyl nitrate solutions. Ten final reports have been issued. In addition, Argonne National Laboratory - West also analyzed these solutions for elemental concentration utilizing IDMS.

Besides their use in the SME Program, the uranyl nitrate solutions, both those characterized for elemental assay and those characterized for isotopic distribution, may be used in cooperation with the Safeguards Assessment Program for performance tests during periodic MC&A inspections.

Uranium Oxide (UO_3) Material

This material is used to assess the ability of the participating facilities to analyze hygroscopic materials. NBL and the Y-12 Plant agreed to participate in the analysis of this material; because of the curtailment of activities at Y-12, only NBL was able to report results. Two final reports were issued.

Uranium Hexafluoride Material

Previously, Portsmouth GDP assisted NBL in the construction of a UF_6 sampling manifold and donated several 2S cylinders of UF_6 to the SME Program. The material was distributed to NBL, Paducah GDP, and Portsmouth GDP. Ten reports were issued to these facilities and the respective Operations Office.

Next fiscal year, the NRC will be supporting the inclusion of the gaseous diffusion plants in the Program. In preparation for their continued participation, a two-year supply of UF_6 was packaged into P-10 tubes for later distribution.

Plutonium Materials

A new solution prepared from a plutonium isotopic CRM was added to the Program this year; there are now three plutonium isotopic solutions available in the Program. Last year, a single test sample set was sent out to participants. A quarterly report summarizing comparative data from all participants on the first test sample set was prepared and distributed in FY 95.

This fiscal year, a full shipment including four quarters of samples was distributed to participants. LANL, NBL, Savannah River Plant, and Westinghouse Hanford have submitted results. Five final reports were issued to the facilities and cognizant Operations Offices through September, 1995.

Papers and Meetings

Mr. Michael Soriano of NBL's Numerical Analysis Group presented a paper on SME Program statistical data analysis at the annual meeting of the Central Region of the Institute of Nuclear Materials Management. The Program Manager presented similar information at the Calorimetry Exchange annual meeting.

Plans for FY 96

The Measurement Evaluation Program will conduct a meeting of participants in October, 1995 and will prepare and distribute a comparative report covering uranium results submitted in FY 92 through FY 94.

Because of the end of the "cold war," many nuclear materials are being moved into storage. NDA will be utilized to measure these materials to reduce exposure, and to avoid opening the storage containers for removal of samples for destructive analysis. Construction and characterization of a series of uranium NDA gamma standards are planned for next fiscal year, to be used in a "round robin" type of sample exchange.

During this fiscal year, NBL completed a Measurement Development Program project involving plutonium IDMS, funded by EM-334 as a "High Return on Investment" project. As a result of this project, the SME Program will distribute test samples in FY 96 to plutonium participants to be analyzed for total plutonium content by IDMS.

As part of the DOE/OSS efforts to improve efficiency, the Calorimetry Exchange Program will be consolidated within the SME program in FY 96.

Enhancement of the new database application for the statistical evaluation of Program results will continue in FY 96. Plutonium analysis will be incorporated, and the application will be adapted to format and produce comparative annual reports.

DEVELOPMENT OF COMPUTERIZED INTEGRATED SAFEGUARDS SAMPLE EXCHANGE PROGRAM DATABASE APPLICATION

D. T. Baran, M. D. Soriano, M. M. Smith, M. E. Downey, and M. I. Spaletto

Introduction

Through the SME Program, NBL distributes test materials of known composition for analysis of the elemental composition of uranium and of isotopic distribution of both uranium and plutonium. Participating safeguards laboratories submit analytical results to the Program; NBL then performs a statistical evaluation and transmits back to the participants monthly, quarterly, and annual reports. The original process for handling the data and generating the reports had been modified over several years and had become outdated and inefficient. The authors recently developed a database-driven application that streamlines the data entry, statistical analysis, quality assurance, plot and report generation. The development of the new database application was selected as a pilot case study to test methodology of process improvement developed by the CH Management of Process Quality Team.

The Original Process

Figure 1 pictures the original SME Program statistical analysis and report generation process. The process was time-consuming and filled with many places for possible error introduction. Additionally, the process utilized multiple computer systems and outdated software. Data entry was accomplished utilizing a Hewlett-Packard (HP) 3000 computer; reference values for the data were contained in a separately-maintained program.

After data entry, the data file was edited in order to format it for submission to the SME Program statistical analysis computer program, an adaptation of a program used for an earlier sample exchange program. This program had been subjected to several modifications as computer equipment was updated.

The results from the outlier portion of the program were then reviewed, any identified outliers removed, and the data file re-submitted to the program for analysis of variance. Data for final statistical analysis was then submitted from a computer with a plotter attached (not the computer used for data entry). Next, the HP

data was transferred over a personal computer network to a Wordperfect file for further editing to a report format before transferring again to become part of the final statistical report. Additionally, summary statistics were read from the computer output and typed into the report.

At the end point, quality assurance was performed. The checker manually checked all data entry for transcription errors as well as manually checking the report and graphics for both alpha (typos) and numeric errors. If an error was found in the original data entry, the process went back almost to the original starting point for correction.

Multiple years of data generated by multiple facilities in the Program were tracked independently via QuattroPro spreadsheets which required duplicate entry of the original data. The spreadsheets were then manually compiled for year-end final reports comparing results for year-to-year or facility-to-facility.

In summary, the process involved the repeated manual entry of the same data into at least two different computer systems, compounding the likelihood of transcription errors, and increasing human effort. Transcription errors were not found until late in the process, requiring additional time and effort to rerun the statistical package and graphics. Under the original process, long term trend analysis and generation of comparative reports were difficult.

The New Process

Figure 2 pictures the new SME Program data analysis and report generation process. The new process is a streamlined Windows-based, database application running on NBL's personal computer network that unifies all aspects of the process under one application. The new application offers easy entry of data into easily read computer screens. Editing and corrections are easily performed. Quality assurance must be performed to verify data entry before the data can be submitted to the statistical program, which has been re-written in Visual C++ for Windows into two separate routines. The outlier routine flags any suspected outliers, but still permits NBL statisticians to either accept or reject the program's findings. Next, the data set is submitted for an analysis of variance. Finally, directly from the application, the user can generate statistical reports and final-quality graphs of the data set with a few clicks of a mouse and without the risk of errors as was present in the individually-entered information for the graphs and statistical report.

The user, in addition to processing data from participating facilities and generating reports, can enter other important information into the application. This includes information on the physical parameters of uranium

isotopes, such as half-lives and atomic masses; information about the participating facilities; reference value information; and lists of analytical methods used and materials available for analysis. The user may also group data into report packages for current and future statistical analysis. Thus, the new application will permit timely, accurate reports and graphs in a fraction of the time currently needed.

In summary, the new process is a single system application utilizing database structures to store, edit, and analyze data. Additional queries can be made to the entire dataset, allowing for easy production of compiled reports comparing results from year-to-year or facility-to-facility.

Conclusion

The application utilizes the Windows environment exploiting the compatibility of Windows-based applications (FoxPro, Visual C++, QuattroPro for Windows and WordPerfect for Windows) to offer a seamless method to rapidly transfer data from statistical routines to graphs to text files. In addition, the use of a database platform will allow easy generation of multi-year, multi-facility statistical evaluations, graphs and reports. All uranium reference data, both for uranium elemental concentration and for isotopic distribution, have been entered into the database, and parallel testing has begun. The effort to produce this improved process was included as a pilot case study in the CH "Management of Process Quality Guidebook."

In FY 96, plutonium isotopic distribution reference data will be incorporated into the application. Future planned enhancements include direct data entry by the participating facility and preliminary reporting via the Internet.

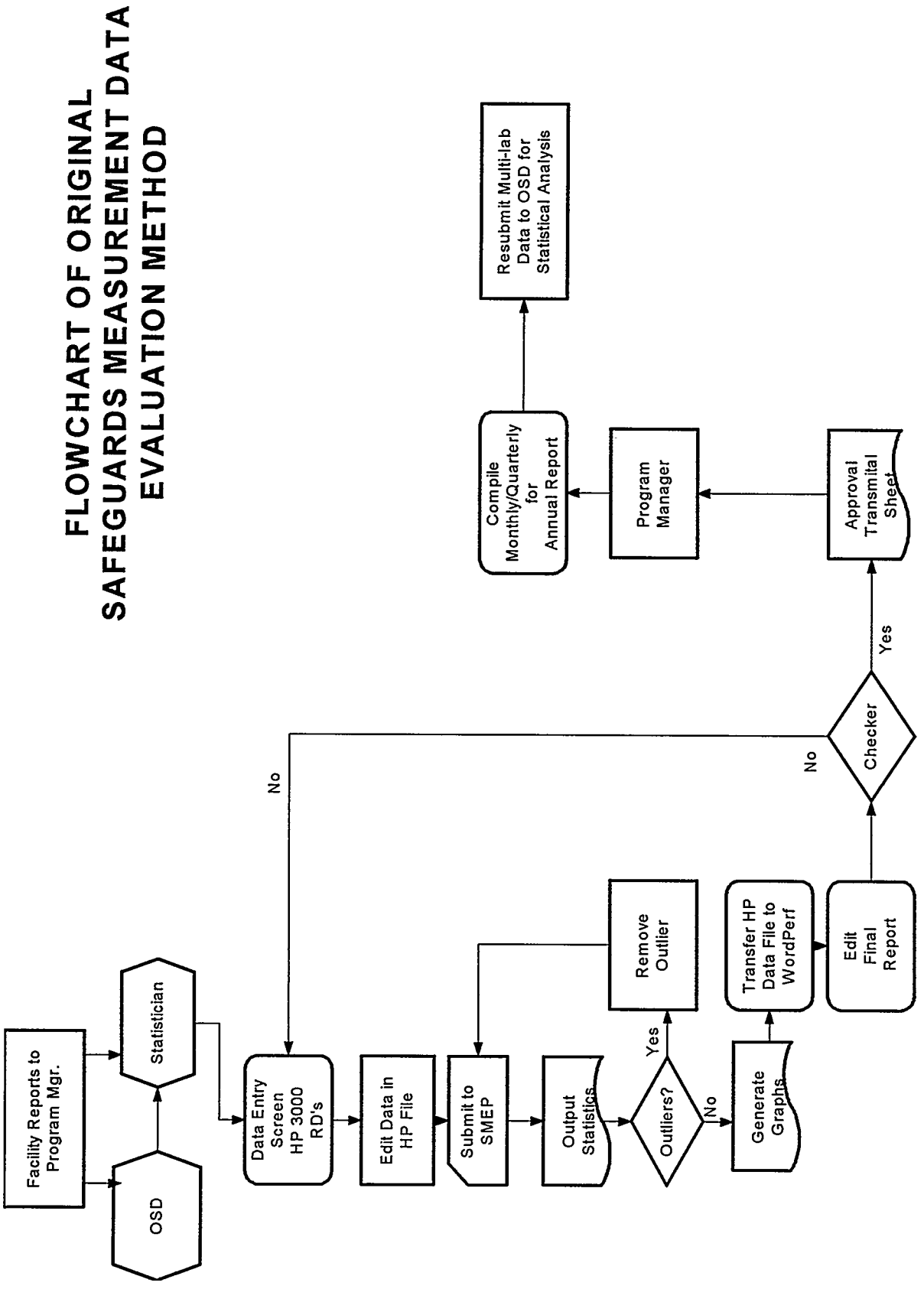
FLOWCHART OF ORIGINAL
SAFEGUARDS MEASUREMENT DATA
EVALUATION METHOD
Facility Reports to Program Mgr.
OSD
Statistician
Data Entry Screen HP 3000 RD's
Edit Data in HP File
Submit to SMEP
Output Statistics
Outliers?
Yes
No
Remove Outlier
Generate Graphs
Transfer HP Data File to WordPerf
Edit Final Report
Checker
No
Yes
Approval Transmittal Sheet
Program Manager
Compile Monthly/Quarterly for Annual Report
Resubmit Multi-lab Data to OSD for Statistical Analysis

Figure 1

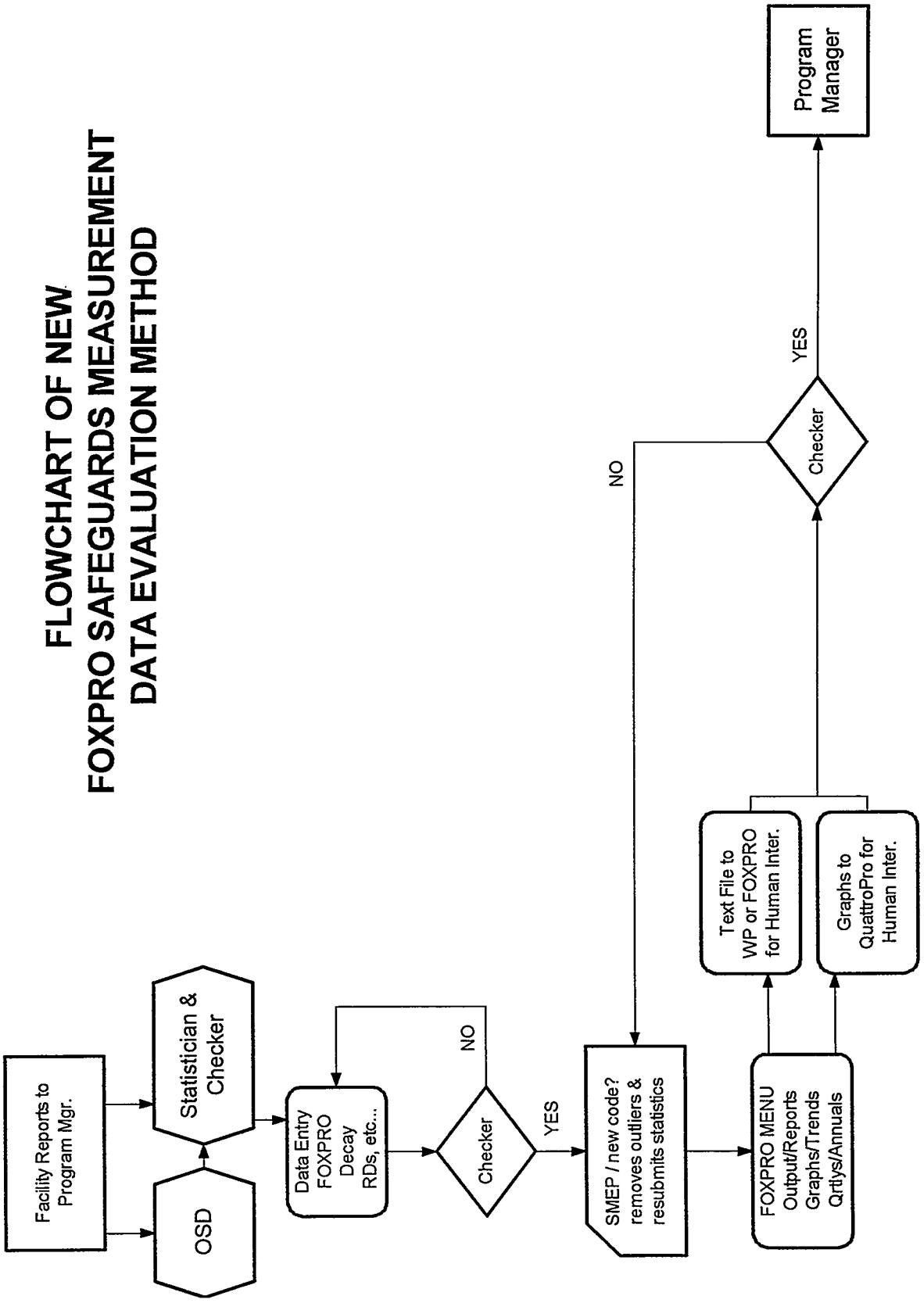
FLOWCHART OF NEW
FOXPRO SAFEGUARDS MEASUREMENT
DATA EVALUATION METHOD
Facility Reports to Program Mgr.
OSD
Statistician & Checker
Data Entry FOXPRO Decay RDs, etc...
Checker
NO
YES
SMEP / new code? removes outliers & resubmits statistics
FOXPRO MENU Output/Reports Graphs/Trends Qrtlys/Annuals
Text File to WP or FOXPRO for Human Inter.
Graphs to QuattroPro for Human Inter.
NO
Checker
YES
Program Manager

Figure 2

MEASUREMENT DEVELOPMENT PROGRAM

U. I. Narayanan and J. P. Zebrowski

Most of the Measurement Development Program projects in recent years have centered on increasing the efficiency and effectiveness of measurement methods, reducing waste produced by the methods, and upgrading and replacing obsolete analytical instrumentation. These projects are necessary for NBL to function as a productive state-of-the art analytical laboratory.

The Pu isotope dilution mass spectroscopy project received EM High Return on Investment funding and the automated coulometric determination of uranium project received funds from EM-334 during FY 95. Significant progress was made on numerous other projects, as described below.

Analytical Methods

Isotope dilution mass spectroscopy was statistically evaluated for use in the chemical assay of plutonium. When implemented, this method will allow accurate determinations of Pu in samples in microgram quantities. This will drastically reduce resultant waste. Additionally, the analysis quantity reduces the interfacility shipping problems when analytical samples are exchanged.

A statistical evaluation of the laser kinetic phosphorimetric analysis of uranium was completed this year. This analysis method is designed to quantify very low levels of uranium in solution. The method has been shown to be capable of a relative standard deviation of $\leq$ 3% for solutions containing 0.001 to 5.0 μg U/g solution. Accuracy within 2% was obtained in this range. The detection limit is 0.02 ppb. A topical report on this method is currently being written.

A procedure was developed for the preparation and the fully automated, semi-quantitative analysis of impurities in samples via x-ray fluorescence spectrometry. This procedure, intended for the analysis of loose powders or samples dried on filter paper, is essentially nondestructive and allows for near-quantitative recovery of the sample. Results will provide analyst information on a samples composition prior to destructive assay.

NBL is continuing its work on the automation of its constant current coulometer for uranium analysis. This method, when used in place of the NBL titrimetric method, will eliminate the chromium in the waste, making

disposal of the waste less difficult and expensive. A bias in the method was observed, and the sources of the bias were identified and eliminated. The method is currently undergoing a statistical evaluation.

The development and testing of a computerized program ("ALPHAFIT") for alpha spectrometric analysis is proceeding. This program is a sophisticated peak-fitting routine for use in determining the isotopic abundances of Pu and U samples. The program uses up to seven parameters per peak fit and up to 12 peaks per region of interest to de-convolute typical complicated Pu alpha spectra.

Analytical Instrumentation

NBL has purchased and installed a new ICP-AES to replace an outdated instrument. The instrument, a Liberty 110 purchased from Varian, achieves better resolution and lower detection limits than the NBL's previous instrument. The computer controlled operation also improves efficiency of analyses by allowing unattended operation, including all quality control measurements.

Procedures were developed and refined for in-field nondestructive assay measurements using a portable gamma-ray spectrometer equipped with a NaI detector system. With these procedures, hold-up measurements were performed on NBL drain lines, and on GE Wilmington HEPA filters. The instrument was also used to perform field enrichment measurements of GE Wilmington pellet, powder, and ash samples.

In FY 94, glovebox installation of a VG/Fisons PlasmaQuad PQ2+ ICP-MS was completed. This year, work has centered on optimization and performance testing of the instrument and the preparation of standard operating procedures and safety documents. When this work is completed, the analysis of low level impurities in samples containing both uranium and plutonium will be possible using the ICP-MS.

Training

A summer student, appointed to the Summer 1995 Student Research Participation Program at Argonne National Laboratory, participated in Measurement Development Program Activities at NBL. This program benefitted both the laboratory and the student, since NBL received additional assistance on a development project, while the student received experience in a working analytical laboratory.

Publications and Presentations

Three NBL Topical Reports, providing detailed descriptions of completed projects, were completed and externally distributed during FY 95. The three topical reports are; "Database Application for Input and

Review of Information on Analytical Measurements", "The Quantitative Ion Exchange Separation of Uranium from Impurities", and "Evaluation on the use of Cerium in the NBL Titrimetric Method".

Three posters were presented at a poster session of the First Annual Strategic Environmental Research and Development Conference Program (SERDP) Conference in Washington, D.C.. These were; "The Quantitative Ion-Exchange Separation of Uranium from Impurities", "Isotopic Dilution Mass Spectrometric Analysis of Uranium", and "Database Application for Input and Review of Information on Analytical Measurements". All three projects had received funding from SERDP during FY 94.

Two posters were presented at the poster session of the DOE Pollution Prevention Conference XI, held in Knoxville, TN. The posters presented were "Evaluation of the Use of Cerium in the NBL Titrimetric Method" and "Database Application for Input and Review of Information on Analytical Measurements".

A paper, "Uranium Isotope Dilution Mass Spectrometry", and two posters, "Database Application for Input and Review of Information on Analytical Measurements" and "Plutonium Isotopic Abundance from Alpha Spectroscopy", were presented at the annual INMM meeting in Palm Desert, CA.

USE OF THE INSPECTOR FOR IN-FIELD NON-DESTRUCTIVE ASSAY AND HOLD-UP MEASUREMENTS

D. T. Baran and G. A. Sowell

Introduction

In response to IAEA inspections of DOE facilities in the United States, NBL purchased a portable NDA instrument to perform in-field support of DOE or NRC safeguards assessment activities. Field measurements were performed to determine the enrichment of GE Wilmington pellet, powder, and residue ash samples. In addition, techniques were developed to perform hold-up measurements of potential deposits of material that cannot be easily measured by any other method. Hold-up measurements were performed on NBL drain lines and on GE Wilmington HEPA filter arrays.

Background

In general, γ-ray spectroscopy is a quick and inexpensive, non-destructive method for measuring some nuclear characteristic of special nuclear material. A system calibrated for energy can positively identify the presence of isotopes of importance such as ^{235}U, ^{239}Pu, and ^{241}Am. In addition, if the system is also

calibrated against well-characterized standards, the system can perform mass and/or ^{235}U enrichment assays, often to within 5%. For enrichment calculations, NBL utilizes the "enrichment meter" principle given by

$$Enrichment = A(ROI1) + B(ROI2) \quad (1)$$

where Enrichment is the ^{235}U enrichment in percent, ROI1 is the total counts of the spectrum between 170 and 200 keV (this contains the strong 235U γ-ray peak at 185.7 kev), ROI2 is the total counts of the spectrum between 200 and 230 keV (this is essentially a background region), and A and B are calibration constants.

Finally, the system can be calibrated against a well-characterized point source utilizing the LANL hold-up measurement technique in order to assay mass amounts configured in a variety of distributions. These hold-up measurements by their vary nature often contain large (>50%) uncertainties but offer a method to measure material located in inaccessible locations.

Enrichment Results

The InSpector system was utilized at the GE-Wilmington Fuel Fabrication Plant during an NRC inspection in order to verify the material lot sample enrichments. The system showed excellent agreement between stated enrichments and measured enrichments for all the powder and ash samples and in 8 of 9 pellet measurements. Table I summarizes these results. One pellet (indicated by an asterisk on Table I) measurement showed a difference of 2.01 standard deviations between the stated and measured enrichment. This sample was flagged by the NRC and GE for further analysis. The uncertainty shown in the measured 235U in Table I represents one sigma. ROI1 and ROI2 were described above.

Hold-up Measurements Results

References 1 and 2 provide the details of hold-up measurements. The actual calibration allows the determination of calibration constants for a point, line, and area source. Using some knowledge about the actual item being assayed, an educated inference can be made as to the material distribution and which calibration set should be used.

TABLE I

GE-WILMINGTON DATA

Type	Sample #	ROI1	ROI2	Measured % ^{235}U	Stated % ^{235}U
background		38589	10546		
background		37750	10094		
background		40461	11024		
background		36186	9772		
pellet	667	51294	13441	4.30 ± 0.53	4.901
*pellet	670	47899	13291	2.66 ± 0.42	3.505
pellet	673	48913	15929	1.10 ± 0.50	0.71
pellet	666	50212	14114	3.21 ± 0.51	2.605
pellet	674	45955	14632	0.60 ± 0.39	0.71
pellet	664	48014	14283	1.94 ± 0.44	1.604
pellet	669	49941	14586	2.69 ± 0.51	2.207
pellet	668	53365	14335	4.66 ± 0.62	4.405
pellet	665	51865	14098	4.07 ± 0.56	3.957
powder	715	61132	15462	4.72 ± 0.53	4.9
powder	716	53019	14773	2.56 ± 0.36	2.45
powder	713	50552	15425	1.53 ± 0.31	1.6
powder	717	57109	13840	4.20 ± 0.44	4.4
powder	712	56745	15631	3.32 ± 0.44	3.2
powder	714	60460	15202	4.63 ± 0.51	4.405
ash	738	39217	10122	---	0.008
ash	739	42410	10459	---	0.009
ash	740	58329	14837	4.14 ± 0.47	3.953

The filter array measured at GE Wilmington consisted of a 1/8" Al plate on the bottom of the HEPA filter array, and 1/8" Fe plate on the top of the HEPA array. The HEPA filters were measured to be 27" X 27". Top measurement distance (looking down) between the array and the detector was 14", bottom measurement distance (looking up) between the array and detector was 19". The calibration utilized a 9.17g UO_2 pellet of 3.957% enrichment for a ^{235}U mass of 0.319 g. Spacing between calibration points was 6" and the distance from the detector to the measurement line was 6". This calibration led to a hold-up value of the HEPA filter array at GE-Wilmington, of 13 ± 8 grams of uranium. Based upon historical averages and previous clean-out time, personnel at GE-Wilmington estimated the amount of uranium in the HEPA filter to be approximately 20 grams.

In addition to the GE-Wilmington HEPA filter measurement, hold-up measurements were performed at NBL of eight requested drain traps. Results are shown in Table II.

TABLE II

NBL HOLD-UP RESULTS

Location	Grams ^{235}U in Trap
C146	0.109 ± 0.034
D214	0.018 ± 0.010
C238	0.045 ± 0.016
C250 N	0.076 ± 0.025
C250 C	2.258 ± 0.657
C250 S	0.565 ± 0.165
C234 A	0.083 ± 0.027
C158	2.847 ± 0.752

The traps in C250 C and C158 had been identified by health physicists to be the "hottest" As yet, no definitive results from the trap clean out have been obtained to compare to the hold-up measurements.

DEVELOPMENT OF PLUTONIUM ISOTOPE DILUTION MASS SPECTROMETRY FOR ROUTINE ANALYSIS

U. I. Narayanan, F. E. Jones, A. V. Stiffin, M. I. Spaletto, M. D. Soriano, M. A. Legel, and D. E. Dallmann

Introduction

Plutonium isotope dilution mass spectrometry (Pu-IDMS) is an analytical method used to determine total plutonium content in samples. The driver to develop this method as one of the routine methods of analysis at the NBL is based on the advantages it offers because of the small sample size needed for analysis, compared to traditional methods. The use of this method results in minimized waste production; additionally, the need for only microgram quantities of sample for analysis drastically reduces problems associated with shipment of material across the complex. This therefore facilitates exchange and measurement of plutonium samples across the nuclear complex, which is vital for nuclear safeguards.

This method is performed by adding a "spike", a known amount of a plutonium material consisting almost exclusively of a single isotope present in low amounts in typical plutonium materials, to plutonium samples which consist primarily of ^{239}Pu. After the addition of the spike, it is essential that the sample and the spike be completely mixed to ensure that all plutonium isotopes are in the same chemical form, referred to as isotopic equilibrium. This is usually accomplished by performing oxidation-reduction reactions on the plutonium in the mix.

Two different methods of isotopic equilibration were tested. The first method involves reducing the plutonium in the mix in 8 *M* HNO_3 by adding 30% hydrogen peroxide; re-oxidation is accomplished by heating the mix until the peroxide is decomposed. The hydrogen peroxide method is effective in relatively pure samples, and has the advantage of not introducing any other elements into the mix. The second method involves reducing the plutonium in the mix in 3 *M* HNO_3 by adding ferrous ion; re-oxidation is accomplished by raising the normality of the mix to 8 *M* by the addition of concentrated HNO_3. This method is more suitable for less pure plutonium samples, especially those containing transition elements. Both isotopic equilibrium methods were tested so that the Pu-IDMS method developed would have wider applicability.

The plutonium was subsequently isolated from the matrix by ion exchange to remove interfering isobars. A mass spectrometric plutonium isotopic analysis was performed on the cleaned mixture. The observed dilution of the tracer plutonium isotope was then used to calculate the original total plutonium content in the sample.

Preliminary Experimental Design

Much thought was devoted to the selection of apparatus, experimental design and conditions to maximize the precision and accuracy of the method and to achieve waste minimization. In preliminary studies, reagent blanks were monitored, sample size and Pu concentration of the mixes were varied, and analysis of mixes with and without ion exchange were performed. Results from these limited studies indicated that these variations did not affect the performance of the method.

Procedure

All plutonium test materials used were NBL CRMs traceable to the national measurement base. The spike was CRM 130, Plutonium Spike Assay and Isotopic Standard, which is 99.94% ^{242}Pu. Two other CRMs of known Pu concentration and differing isotopic compositions were chosen to be representative of sample types in the industry. The first sample material was CRM 126, Plutonium Metal, with an isotopic composition of 99.9% ^{239}Pu; this sample is representative of weapons grade plutonium. The second sample material was CRM 122, Plutonium Oxide, with an isotopic composition of 87% ^{239}Pu and 11.5% ^{240}Pu; this sample is representative of other grades of Pu, such as nuclear reactor grade.

Following a statistical plan, mixes were prepared for analysis. The plan was designed to study the effects and/or the potential sources of variation from the two sample materials and the method of isotopic equilibration. Each mix consisted of a known quantity of CRM 130 spiked into prepared solutions of either CRM 126 or CRM 122 of known concentration. The spike-sample mixes were prepared to give a mix with a 1:1 ratio of ^{242}Pu to ^{239}Pu, containing about 100 μg total Pu. This ratio is known to give the most accurate results. The mixes were then subjected to one of the two methods of isotopic equilibrium that were used in this study.

Following a statistical scheme of analysis, the isotopic measurements were performed on a Finnigan MAT 261 mass spectrometer equipped with an adjustable multi-cup Faraday array for simultaneous ion collection. 200 ng Pu were loaded onto degassed rhenium filaments and into the instrument, which contains a 13-sample turret assembly. Instrument operations were controlled automatically with a Hewlett Packard Model 310 computer. CRM 128, Plutonium-239/Plutonium-242, 1:1 Atom Ratio, was used to calculate the mass discrimination factor, to compensate for the preferential evaporation of lighter isotopes. The same CRM was also used as a quality control standard. QC aliquants of this CRM were subjected to the same treatment as the samples, including both methods of isotopic equilibration, to ensure that the chemical treatment did not affect isotopic results. No effect was seen, and the mean of the percent relative differences of the

measured ratio *versus* the certified ratio was ±0.05%, well within the laboratory quality control limits of ±0.15%. Turret-to-turret variation was also estimated using the results of the QC aliquants on each turret.

The total quantity of plutonium in the sample was then calculated by using standard IDMS equations below.

$$R_{ik} = \frac{A_i a + B_i b}{A_k a + B_k b}$$

where: R_{ik} = atom ratio abundance of isotopes i and k for the sample-spike mixture
A_i = atom fraction i in sample
B_i = atom fraction i in spike
A_k = atom fraction k in sample
B_k = atom fraction k in spike
a = moles of element in sample
b = moles of element in spike

Solving for a, moles of the element in the sample was determined using the formula:

$$a = \frac{b\ (B_i - R_{ik}B_k)}{R_{ik}A_k - A_i}$$

The concentration of the sample was then calculated by multiplying "a" by the gram-atomic-weight of the element in the sample and then dividing by the weight of the sample in the aliquant.

The calculated value was compared to the known plutonium content of the sample to quantify method performance.

Results and Discussion

The results of this study are summarized in Table I. The first column identifies the sample used to make the mixes. The second column identifies the isotopic equilibrium method used to treat the mixes. The next three columns contain information on number of samples analyzed in each set, the amount of plutonium determined by IDMS as compared to the known plutonium content of the sample expressed as mean percent relative difference (%RD), and the standard deviation of each mean.

TABLE I

RESULTS OF IDMS ANALYSIS

Sample	Method	n	RD, %	SD, %
C126	Ferrous	4	0.086	0.10
C126	Peroxide	4	-0.116	0.20
C122	Ferrous	4	-0.045	0.03
C122	Peroxide	4	-0.126	0.17
Combined	**Results**	**16**	**-0.050**	**0.10**

All samples were spiked with CRM 130.

No significant differences were observed because of the sample type, the isotopic equilibrium method, or turret-to-turret variation. Based on this observation, all the data from 16 sample mixes were combined to compute an overall result: the mean %RD was -0.050% with a standard deviation 0.10%.

Conclusion

The plutonium isotope dilution mass spectrometric method was successfully tested and developed for routine use at the laboratory. Two different methods of isotopic equilibration were tested and qualified. The hydrogen peroxide method will be used for relatively pure samples and the ferrous ion method will be used for less pure samples. Procedures were standardized and quality control samples needed for use in this method for plutonium sample analysis were developed. Proper choice of apparatus and experimental methodology lead to considerable waste minimization. The small sample size requirement for this analysis permits the easier shipment and measurement of plutonium samples. The results of the statistical study shows that the method has many advantages in nuclear safeguards applications.

STATISTICAL EVALUATION OF THE LASER KINETIC PHOSPHORIMETRIC ANALYSIS OF URANIUM

P. V. Croatto, I. W. Frank, K. D. Johnson, P. B. Mason, and M. M. Smith

Introduction

As a replacement for the Scintrex UA-3 Uranium Analyzer, NBL has evaluated a commercially-available kinetic phosphorescence analyzer, KPA-11 (Chemchek, Richland, WA). The Chemcheck KPA is a bench-top

instrument which performs single-measurement, quench corrected analyses for trace uranium.[1,2,3] It incorporates patented kinetic phosphorimetry techniques to measure and analyze sample phosphorescence as a function of time. With laser excitation and time corrected photon counting, the KPA has a lower detection limit than other methods. Operated with a personal computer, the state-of-the-art KPA offers extensive time resolution and phosphorescence lifetime capabilities for additional specificity. Interferences are thereby avoided while obtaining precise measurements.

Background

Of the methods used to determine trace quantities of uranium, the most common and most sensitive method is the measurement of its fluorescence. Uranium fluorescence has been measured in liquid media such as sulfuric and phosphoric acid, or in disks or pellets after fusion with salts such as sodium fluoride or carbonate.[4,5] Many factors affect the fluorescence in fused pellets. The fusion requires strictly regulated conditions of flux composition, heating time, and temperature. The method is lengthy, usually involving separations and extractions to remove interfering elements. Conventional fluorescence measurements made directly in solution are very sensitive to quenching by many different ions and also by organic material; the sensitivity is only about 1 μg U/mL in comparison to about 0.1 ng U/mL of sample using the fusion methods. The identification and control of some of the many variables of the procedure have allowed some laboratories to obtain precisions of 10-12%.[6]

A significant breakthrough in the determination of uranium by fluorometry has been achieved through the use of pulsed laser ultraviolet light as the excitation mode. NBL has used the Scintrex UA-3 Uranium Analyzer to analyze low-level uranium samples by this method.[6,7] Measurements with a 2-3% RSD and accurate to better than 1% have been obtained in the 0.01 to 4 μg U/g solution range. The detection limit is 0.05 ppb uranium. It is a direct method requiring no separations, extractions, or fusions and therefore is many times faster than conventional fluorometric methods, each analysis requiring only about 6 minutes. A special feature of the method is the use of a standard addition technique to eliminate sample matrix effects. The disadvantage of this technique is that fluorescence is strongly dependent upon the temperature of the solution; studies show that a 1°C increase causes a 3.5% loss in fluorescence in the 20-25°C range. Accurate results, however, can be achieved by careful heating of the sample solution. In addition, the method requires the use of an internal standard and corrections for anionic enhancement from certain concentrations of acids ($PO4^{-3}$, $SO4^{-2}$, and F^-) have to be made.

As a replacement for the Scintrex UA-3 Uranium Analyzer, NBL has investigated the use of the similar technique of phosphorescence for a fast, sensitive, and accurate method for the determination of uranium. The phosphorimeter evaluated is a commercially-available Kinetic Phosphorescence Analyzer, KPA-11. This instrument uses a pulsed nitrogen/dye laser to supply monochromatic ultraviolet light to excite uranium atoms in the sample solution. These atoms then emit a green phosphorescence which is filtered, amplified, and measured. To protect the uranyl ion from quenching, a phosphate-based complexing reagent is added which yields phosphorescence lifetimes for UO_2^{2+} of a few hundred microseconds. The KPA incorporates kinetic phosphorimetry techniques in a computerized system. The kinetic analysis of the uranyl phosphorescence provides highly precise and accurate measurements, thus eliminating the need for internal standards as in the NBL fluorometric procedure. The system takes phosphorescence measurements during multiple time gates, analyzes the kinetics of the phosphorescence decay, and calculates the result in terms of selected units. The KPA performs a background correction and automatically corrects for most sample quenching from sample matrix effects. Chemical separations are only required for the determination of very low levels of uranium in samples with a substantially complex matrix. In addition, a reference measurement normalizes the sample measurements for internal fluctuations such as laser brightness, temperature drifts, electrical line surges, and high voltage drifts. No temperature control of the sample is needed as in the present NBL fluorometric method.

The KPA instrument has been modified by replacing the europium emission filter used for the measurement of the reference with a uranium emission filter. This allows for the preparation of an "in-house" reference and better measurement control. In addition, the use of disposable plastic cuvettes was evaluated and shown to be both economical, practical, and acceptable for concentrations above 1×10^{-3} μg U/g solution. The instrument has been calibrated (over two ranges) to cover the concentration range of 1×10^{-3} to 5.0 μg U/g solution. Standard solutions containing uranium were analyzed, ranging in concentration from the detection limit of 2×10^{-5} up to 50 μg U/g. The linear and optimal range of response was determined to be from 1×10^{-3} to 2×10^{-2} μg U/g solution for the low range and from 0.5 to 5 μg U/g solution for the high range.

Results

The statistical evaluation part of this project has been completed. The method was validated by three analysts performing measurements over a series of three days analyzing 72 samples, 18 knowns, and 36 blinds for the entire study. This method has been shown to be capable of a relative standard deviation of $\leq$ 3% for solutions containing 0.001 to 5.0 μg U/g solution. Accuracy within 2% was obtained in this range.

The detection limit is 0.02 ppb. All measurements were made in duplicate. The arithmetic mean of the two measurements was then determined and designated as the final assay value of the sample.

The combined data set of sample measurements shows the range of %RDs to be from -8.31% to 2.23% for samples at the High-Level and from -10.28% to 5.38% for the samples at the Low-Level. A summary of the sample data for all analysts combined is shown, by level and in total, in Table I.

TABLE I

SUMMARY OF HIGH AND LOW LEVEL SAMPLE DATA

	n	%RD Mean	Standard Deviation	95% Conf Interval
High Level	36	-2.635	2.784	0.942
Low Level	36	-1.329	3.808	1.289
Combined	**72**	**-1.982**	**3.377**	**0.794**

The negative bias for all measurement groups is evident by looking at the means plus/minus the 95% confidence intervals of the mean. These sample measurements generally have a negative bias of about 2%. Neither the Day-to-Day variation nor the difference between High- and Low-level samples is significant in the combined data set.

Conclusion

Routine analyses can be easily and effectively accomplished, with the accuracy and precision equivalent to the present NBL fluorometric determination and without the need for internal standards. Applications of kinetic phosphorimetry at NBL include the measurement of trace uranium level in retention tank samples and waste samples, the measurement of nanogram uranium contamination (in blanks) in isotopic sample preparations, and the determination of elution curves of different ion exchange resins for uranium purification. In these cases, the samples are fumed twice with nitric acid and redissolved and diluted to an appropriate volume with 1 *M* HNO_3 before measurement. Even though the concentrations are determined on a weight basis, no density corrections are needed since all the samples (including the samples used for calibration) are in the same density matrix (1 *M* HNO_3).

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SEMIQUANTITATIVE NON-DESTRUCTIVE ANALYSIS OF SOLIDS BY WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

J. P. Zebrowski, G. A. Sowell, and R. A. Mason

NBL, as part of its nuclear materials measurement functions, performs uranium and plutonium assay measurements on a wide range of sample materials. The presence of impurities within samples can have an adverse affect on sample preparations or chemical analyses. Since knowledge of a samples content prior to destructive analysis would aid in the planning of analyses, a procedure was developed for the preparation and fully automated, semi-quantitative analysis of impurities in samples via x-ray fluorescence spectrometry. This procedure, intended for the analysis of loose powders or samples dried on filter paper, is essentially nondestructive and allows for near-quantitative recovery of the sample.

NBL presently has a Rigaku RIX 3000 wavelength dispersive x-ray fluorescence spectrometer equipped with a vacuum pump, OS2 platform, RIX 3000 software, a Haskris chiller, and a 6 sample autosampler. The instrument initially scans the energy spectrum and identifies the elements present in the sample. The instrument software then performs on-line semi-quantitative analysis of the measured intensities without the

use of standards by using a fundamental parameters approach. Results are given in terms of weight % of each element detected. Analyses are performed under vacuum conditions. Data acquisition, calculation of results, and report generation are all performed automatically and are all controlled through the Rigaku software.

An important aspect of the procedure is the sample preparation since it involves handling loose radioactive powders. The sample preparation steps, outlined below, have been approved for use. Briefly, the sample is sandwiched between two layers of Prolene® thin film and introduced into the x-ray fluorescence spectrometer. A Po-210 sealed source static remover is required to minimize the risk of contamination due to spread of the sample caused by static charge buildup on the thin film and powder. Samples prepared this way can be analyzed for the presence of elements between Na and Am.

Various powdered samples of known composition were analyzed using the procedure. The results of the analyses indicate that the instrument is effectively able to identify most elements present at 0.3% or above. A few limitations in the procedure should be noted. The x-ray analysis cannot be used to detect the presence of F or lighter elements since the presence of the Prolene® thin film effectively attenuates the characteristic x-rays of these elements, nor can the presence of Rh be detected since the x-ray tube has a Rh target. Inhomogeneity and surface effects may effect the accuracy and precision of the results obtained on powders and filter papers. Because this procedure requires the computer to identify spectral lines, there may be instances due to spectral complexity that an element present in the sample is not identified. Overall, the initial testing indicates that this procedure works effectively as a screening procedure prior to dissolution or further analysis.

AUTOMATION OF THE NBL CONSTANT CURRENT COULOMETER

P. V. Croatto, P. B. Mason, H. D. Troutman, K. D. Johnson, I. W. Frank, and M. M. Smith

Introduction

An alternative to the use of potassium dichromate as a titrant in the NBL Titrimetric Method[1] for uranium analysis was sought since the presence of chromium results in a mixed waste and makes disposal of the waste difficult. The development of an automated version of the NBL constant current coulometer[2] based on the work of Goldbeck and Lerner[3] was evaluated. The building and programming of the automated system along with an evaluation of the method using 20-40 mg quantities of uranium has been completed.

Preliminary results obtained with this system gave a precision of 0.1% RSD with very few outliers or overtitrations. While these results were good and the automation simplified the titration and minimized titration errors, a bias was present. This problem was investigated and the sources of the bias were found to be due to hardware/software problems and the endpoint determination. The bias problem has been resolved and the method is currently undergoing a statistical evaluation.

Automated Coulometer

The NBL automated constant current coulometer consists of a Kepco constant current source with a digital programmer and Hewlett Packard VXI components [multimeter, switches (current relay and multiplexer), universal counter, pulse generator] integrated into a mainframe and interfaced to a HP PC Vectra instrument controller. The instrument control software is written in HP BASIC/BASIC Plus Version 6.2. HP BASIC Plus adds a set of additional keywords to HP BASIC that simplify ease the creation of sophisticated graphical displays and human interfaces.

Results

Preliminary results obtained with this system gave a precision of 0.1% RSD with very few outliers or overtitrations. While the precision was good, the results had a very large bias of approximately +2.57%. Part of the biased was traced to the current measurement which was in error by +1.26%. This was verified by using a separate external ammeter in series in the cathode/anode electrode circuit, measuring the current during a titration run, and comparing the result with the coulometer value for current. It was found that the measured value for the current was incorrect due to an incorrect resistance measurement. This was due to improper grounding in the relay switching multiplexer for the 4-wire Ohm measurement and was easily corrected.

Another problem was in the initial choice of 611 mV indicator electrode potential as the end-point in the titration. This was the value used in the manual coulometric method.[2] The end-point in the automated coulometric titration was at approximately 585 mV as determined from the inflection point in several titration curves. This is also the end-point used in the NBL-Modified Davies and Gray Titration.[1] This difference in end-points (611 mV versus 585 mV) contributed approximately +0.25% to the bias. The end-point was changed from 611 mV to 585 mV in the program.

The remaining bias was caused by a transcription error in the program in the formula to determine the uranium assay and was corrected. The resulting value was off by a factor of 1/resistance (1/0.989 Ohms) which contributed +1.01% to the bias.

The total of the three sources of bias is +2.52% which accounts for most of the bias in the results (+2.57%) of the preliminary sample measurements. With the corrections made to the hardware and software as described above, the system will be statistically evaluated to determine precision, accuracy, and variations (analyst-to-analyst, day-to-day, and blind-to-known) by measuring over a total of 90 samples using three analysts. No statistically significant bias is anticipated.

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PLUTONIUM ISOTOPIC ASSAY FROM ALPHA SPECTROSCOPY

D. T. Baran

Introduction

The development and testing is continuing on a computerized program ALPHAFIT, a sophisticated peak-fitting routine for use in determining the isotopic abundances of Pu and U samples. The program uses up to seven parameters per peak fit and up to 12 peaks per region of interest to de-convolute typical complicated Pu alpha spectra. Recent developments in Si surface barrier detectors, and associated electronics permit alpha spectra to be obtained with 10 to 15 keV resolution. In addition, faster and more powerful computers permit sophisticated peak-fitting and peak de-convolution of multipeak (>10 peaks) regions in a relatively short period of time (< 10 minutes). With a thin layer, electro-deposited sample planchet, a relatively large distance between the detector and the planchet (>15 mm), and long counting times (> 4 hours), one can obtain spectra free of large straggling effects. With these spectra, one can perform the peak fitting and calculate the isotopic abundances.

Background

The peak area due to a specific alpha emitted from a given isotope can be written as:

$$C(E_{ij}) = \frac{N_i BR_{ij} ge(E_j)\, de(E_j) \ln(2)}{\tau_i} \qquad (1)$$

where $C(E_{ij})$ is the peak area of alpha particle j emitted from isotope i, N_i is the number of atoms of isotope i present in the sample, BR_{ij} is the branching ratio of alpha particle j emitted from isotope i, $ge(E_j)$ and $de(E_j)$ are the geometric and detector efficiencies of the system for the detection of a alpha particle with energy E_j, and τ_i is the half life of the isotope i.

For the method in question, it is assumed that the geometric efficiency is constant, i.e., that the layer of material emitting alpha particles is very thin and uniformly distributed. Additionally, it is assumed that the detector efficiency over the range of the emitted alpha particles (4800 kev to 5600 keV) is also constant. With these assumptions, all the peak areas for each isotope are summed and the counts for each isotope are normalized to the total sum, giving the relative abundances of each isotope.

Alphafit

The program utilizes a least-squares fit to the alpha peak shape function combining a parameter space gradient search with an analytical solution developed from linearizing the fitting function[1]. The alpha peak shape is given by[2]:

$$Y_i = Y_0 e^{\frac{-(x_i - x_0)^2}{2[\sigma(x)]^2}} + \delta\{1 - e^{-x^2}\}\{A e^{\beta(x_i - x_0)}\} \qquad (2)$$

where

Y_i is the net counts in channel i,

Y_0 is the peak height at the centroid channel ($x_i = x_0$),

x_0 is the peak centroid channel,

χ^2 is the normalized parameter, given by $((x_i - x_0)/\sigma)^2$,

σ is the Gaussian standard deviation,

$\sigma(x) = \sigma(a(x_i - x_0)^2 + b(x_i - x_0) + 1)$,

A is the tailing amplitudes, β is tailing slopes,

$\delta = 1$ for $x_i < x_0$, and 0 for $x_i > x_0$.

ALPHAFIT fits all peaks from an isotope instead of particular peaks. For example, ^{242}Pu which has a prominent peak at 4900 keV, also has two other peaks, one at 4856 keV and the other at 4754 keV. The program fixes the intensity of the minor peaks to the intensity of the major peak, utilizing the well known alpha branching ratios. Studies on single line alpha sources performed at NBL suggest other parameters, such as σ, a, b, A, and β, are determined by the detector-electronic system and can be fixed for a particular system. Generally, in a multi-peak isotope, only the location, x_0 , the intensity of the major peak, Y_0, and the tailing amplitude, A, are free parameters. This results in three free parameters per isotope instead of up to 35 parameters for an isotope with five peaks.

Once ALPHAFIT determines all the fitting parameters, the program calculates the peak areas for each peak by numerically integrating each individual peak shape function over the range of the spectrum.

Currently, ALPHAFIT divides the Pu alpha spectrum into three regions for peak-fitting. Region One contains 6 peaks, three each from ^{241}Pu and ^{242}Pu. ^{241}Pu does have a small branching ratio for alpha decay (as opposed to β- decay), and given a large enough presence of ^{241}Pu in the spectrum, one can fit these peaks to non-zero values. Region Two is the most complicated region, containing up to 11 peaks of ^{239}Pu and ^{240}Pu. In past alpha spectroscopy systems, it was only possible to sum these two isotopes together, as system resolution was poor. However, higher resolution systems and long counting times enable these two isotopes to be summed separately. Finally, Region Three contains 8 peaks, three from ^{238}Pu and five from ^{241}Am. For freshly prepared samples, where the ^{241}Am has been removed by ion-exchange, this region is essentially all ^{238}Pu and is an excellent region to find the various fixed system parameters. Samples that have aged for three to four years can show significant ^{241}Am activity and give a more complicated region.

Results

The program ALPHAFIT was tested on three existing planchets made from certified reference materials. Tables I, II and III summarize these results.

TABLE I

C128 ASSAYED RESULTS

Isotope	Assay	CRM
238	0.002	0.00364
239	48.190	49.63562
240	0.24	0.3490
241	0.024	0.0215
242	51.55	50.30435

TABLE II

C130 ASSAYED RESULTS

Isotope	Assay	CRM
238	0.003	0.00385
239	0.0	0.00472
240	0.019	0.01956
241	0.146	0.01631
242	99.832	99.95555

TABLE III

C138 ASSAYED RESULTS

Isotope	Assay	CRM
238	0.019	0.00937
239	88.5	91.84278
240	10.0	7.95671
241	1.09	0.1577
242	0.40	0.03343

In general, agreement is good between the measured value and the decay corrected CRM values, with preliminary results showing decent fits for major peaks in the spectrum and calculated isotopic abundances of the major isotopes to ± 4%. Better results are anticipated using freshly prepared, ion-exchanged CRM solutions. Ion-exchanged solutions will eliminate any contribution from ^{241}Am in Region Three.

Figures 1, 2, and 3 show the fits to the data in each region of interest for a typical spectrum. From first glance, the fits seem to be rather poor. These fits are shown on a log scale, emphasizing the poorness of the fit at the end regions. However, these regions contribute very little to the actual peak areas; consequently, they are insignificant in calculating the relative abundances.

Clearly, additional work is required, especially in determining the proper peak shape parameters and in sample preparation. Future work includes upgrading the code to permit more peaks per region of interest. For example, the code currently uses three peaks for ^{239}Pu. Even though the relative peak strengths of other ^{239}Pu alpha energies are small, they contribute to the low energy tail and their inclusion in fitting routines may improve the quality of the fits and ultimately the program's ability to calculate isotopic abundances.

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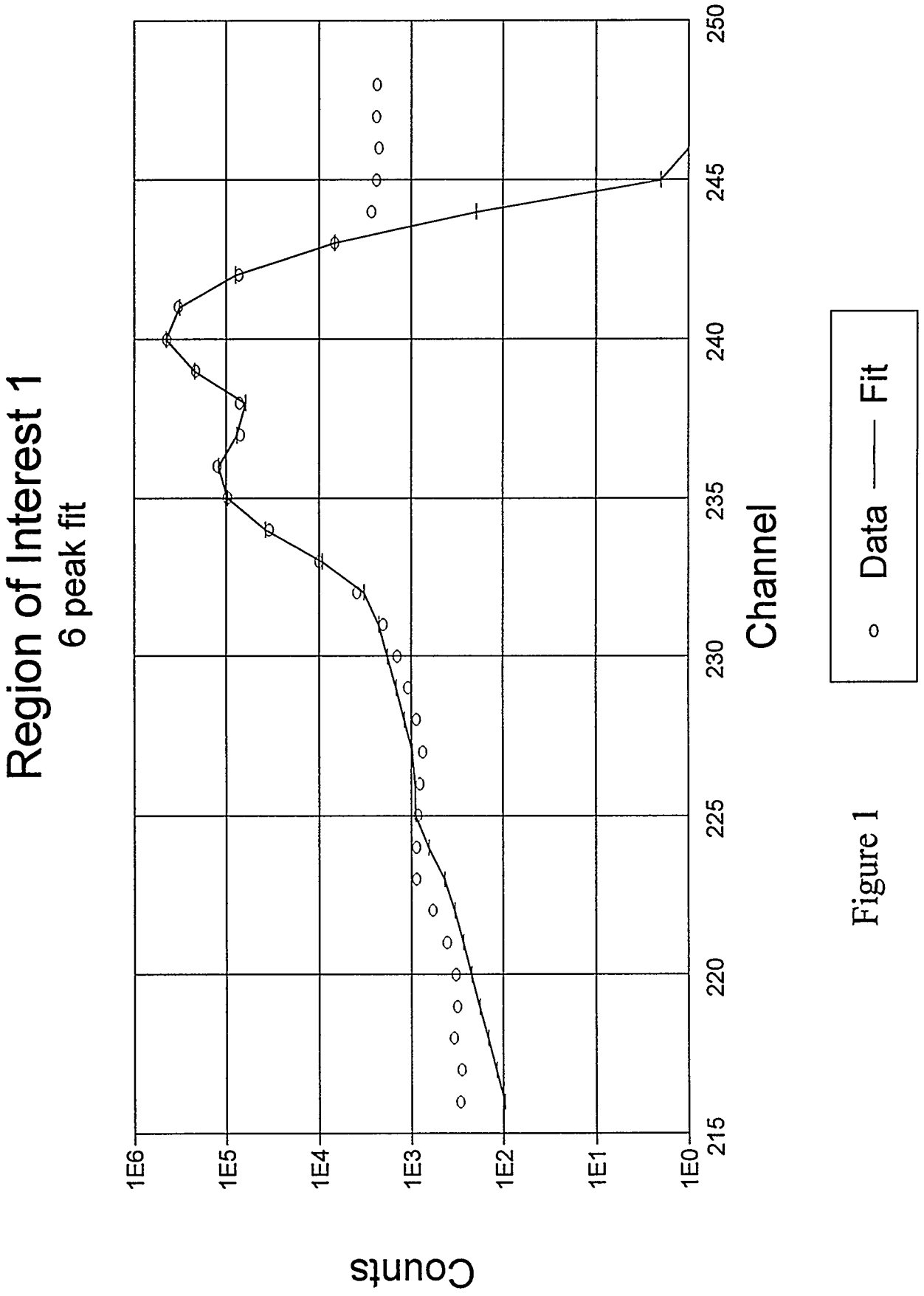
Region of Interest 1
6 peak fit
Counts
1E6
1E5
1E4
1E3
1E2
1E1
1E0
215
220
225
230
235
240
245
250
Channel
Data
Fit

Figure 1

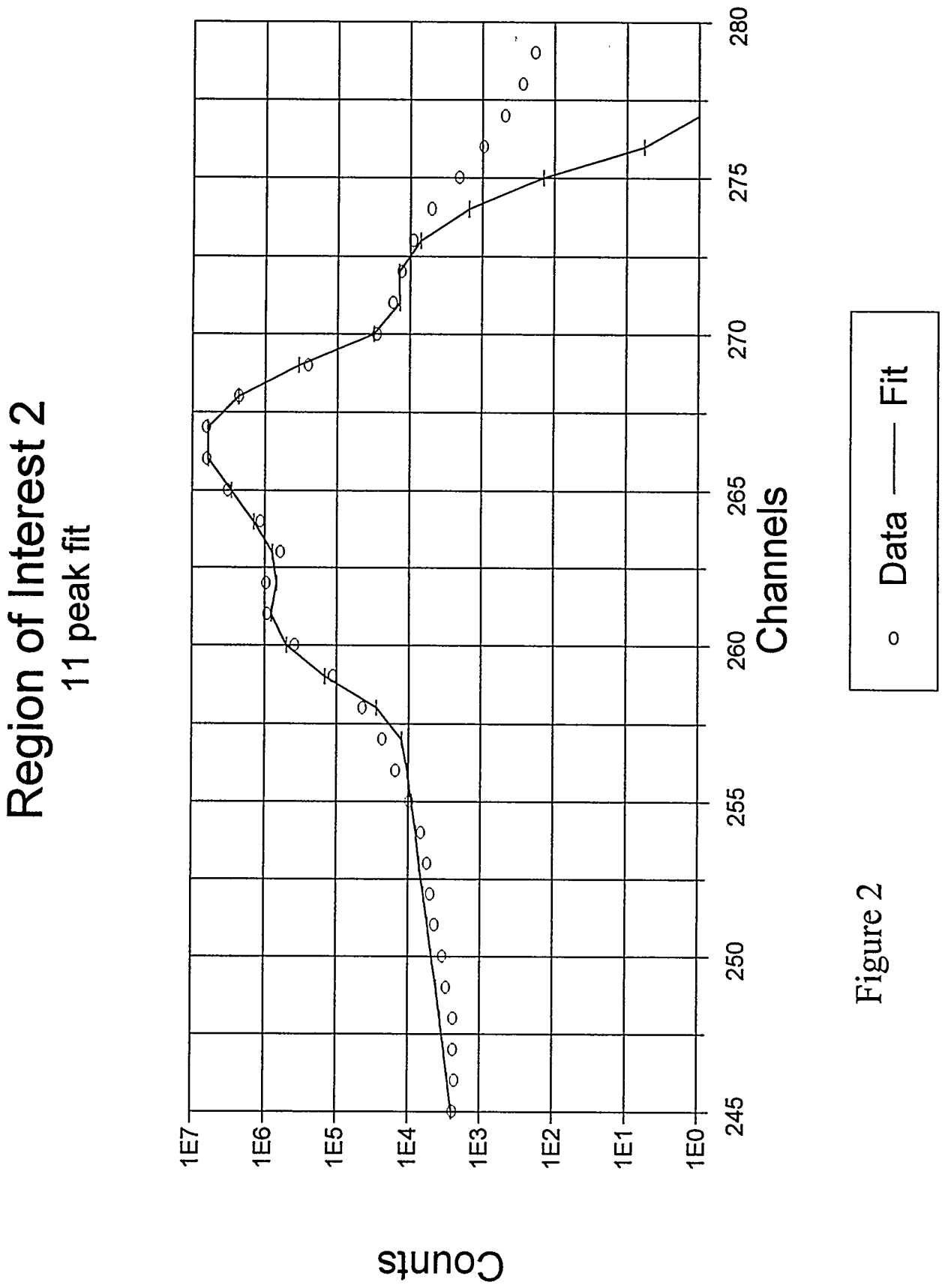
Region of Interest 2
11 peak fit
Counts
1E7
1E6
1E5
1E4
1E3
1E2
1E1
1E0
245
250
255
260
265
270
275
280
Channels
Data
Fit

Figure 2

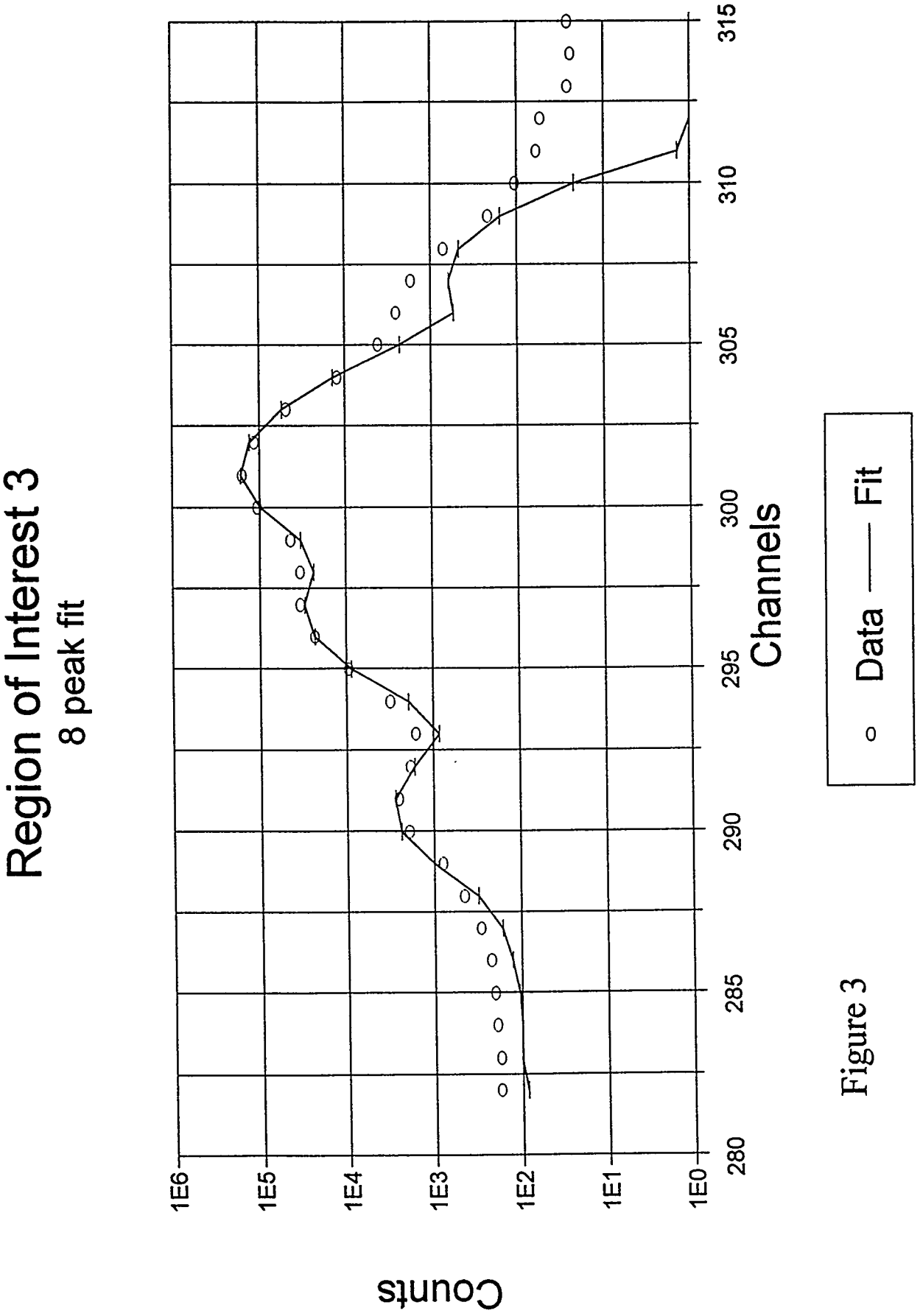
Region of Interest 3
8 peak fit
Counts
1E6
1E5
1E4
1E3
1E2
1E1
1E0
280
285
290
295
300
305
310
315
Channels
Data
Fit

Figure 3

INSTALLATION, ACCEPTANCE AND TRAINING FOR NEW ICP-AES INSTRUMENT

P. B. Mason, J. P. Zebrowski, A. M. Voeks, P. M. Santoliquido, M. J. Rocca, and R. A. Mason

In order for NBL to fulfill its mission as a standards laboratory, it must maintain state-of-the-art analytical equipment. With the breakdown of an existing obsolete ICP-AES, NBL was left without the ability to determine trace and higher-level metal impurities via emission spectroscopy. With the need for this capability, procurement of a new ICP-AES system was initiated and completed. This instruments' primary use will be for characterization of impurities in uranium certified reference materials. Additional applications will be identified and implemented, including possible sample analysis for members of the DOE complex who do not have ICP-AES measurement capabilities.

Following extensive research into a number of commercially available instruments, a Varian Inc. Liberty 110 ICP-AES instrument was selected. This instrument, which is fully computer-controlled, employs a sequential grating spectrometer covering the uv-vis range. Accessories include extensive quality control software, autosampler/dilutor, Meinhard nebulizer, V-groove nebulizer, HF compatible spray chamber, nitrogen purge accessory. This instrument will allow NBL to analyze a wide variety of elements and sample types, with better spectral resolution, lower detection limits, and higher throughput than with the previous instrument, while meeting ever more stringent quality assurance demands.

Preparation of a site for the instrument was completed, with modifications made to the electrical and exhaust systems to meet safety and instrument specifications. The instrument was installed by Varian personnel, with NBL oversight. Training of NBL staff on the use of the instrument included a four day off-site course and eight hours of on-site training for all project members. Following training, acceptance tests were performed indicating adequate resolution and detection limits for several elements, thus meeting the acceptance criteria required by NBL. Work has begun on the optimization of operating conditions, with method development to take place in FY 96 in order to begin sample analysis.

ICP-MS ACQUISITION AND INSTALLATION

A. R. Warren, F. E. Jones, and P. M. Santoliquido

A VG/Fisons PlasmaQuad PQ2+ ICP-MS which was purchased previously has been installed in a glovebox along with an autosampler. This instrument has the potential to do rapid multi-elemental determinations of over 63 elements at levels ranging from parts per thousand to the parts per trillion. For the analysis of impurities in uranium, uranium concentration matched blank and standard solutions will be used to calibrate the instrument in the fully quantitative mode. ICP-MS also lends itself to the measurement of isotope ratios with precisions of 2 - 5%, depending on the relative abundances of the isotopes in question and counting statistics.

During FY 95, work has centered on optimization and performance testing of the instrument and the preparation of standard operating procedures and safety documents. The performance testing of the instrument has been completed; short term precisions of ~1% RSD and detection limits of less than 1 part per billion have been achieved. Standard sample preparation procedures such as the ASTM Method C 1287, "Standard Test Method for Determination of Impurities in Uranium Dioxide by Inductively Coupled Plasma - Mass Spectrometry", are being modified to satisfy NBL standard practices associated with the certification of standard materials. The NBL ICP-MS will be initially used to determine impurity levels in normal uranium; similar determinations for plutonium materials are being planned and will be performed after written procedures for the analysis of uranium materials have been completed.

MEASUREMENT SERVICES PROGRAM

A. V. Stiffin and I. W. Frank

NBL, as the Government's Nuclear Material Measurement and Standards Laboratory, supports nuclear safeguards programs by providing independent measurements on a variety of nuclear materials. NBL serves as a technical extension of the Headquarters Office of Safeguards and Security and provides services on a contractual basis to the NRC. During FY 95, NBL received 96 uranium samples and 16 plutonium samples for analysis. A wide variety of analyses, such as titrimetry, gamma spectrometry, and mass spectrometry were performed on these samples.

New Brunswick participated in the IRMM REIMEP rounds on UO_2 and uranyl nitrate solutions. NBL received two uranyl nitrate solutions and one UO_2 powder sample.

New Brunswick provided measurement services assistance to ABACC by performing isotopic assays to characterize a U_3O_8 material to be used as a secondary standard in the agency's sample exchange program.

The NRC Office of Nuclear Materials Safety and Safeguards (NRC/NMSS) submitted a total of 40 uranium samples for materials verification under the Nuclear Materials Safeguards Program. These samples included pure product materials such as UO_2 powders and pellets, UNH solutions, and ash samples.

There were 50 uranium samples and 16 plutonium samples received as part of NBL's participation in sample exchange programs. They consisted of 32 uranyl nitrate solution samples, 10 UO_3 powder samples, 8 UF_6 samples, 8 plutonium nitrate samples and 8 plutonium sulfate samples received from the NBL SME Program. NBL participates in the SME Program not only to meet requirements for participation in a sample exchange program, but also to evaluate the stability and integrity of sample materials utilized in the SME Program.

In FY 96, NBL will be providing assistance to the NRC in the characterization of the SAPPHIRE materials acquired from Kazakstan.

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