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PROGRESS REPORT

**OCTOBER 1992
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SEPTEMBER 1993**

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U. S. DEPARTMENT OF ENERGY

CHICAGO OPERATIONS OFFICE

NEW BRUNSWICK LABORATORY

CARLETON D. BINGHAM, DIRECTOR

PROGRESS REPORT

OCTOBER 1992

THROUGH

SEPTEMBER 1993

DOE RESEARCH AND DEVELOPMENT REPORT

APRIL 1994

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ABSTRACT

The mission of the New Brunswick Laboratory of the U. S. Department of Energy (DOE) is to provide and maintain a nuclear material measurements and standards laboratory as a technical response to DOE's statutory responsibility to assure the safeguarding of nuclear materials. This report summarizes the mission-fulfilling activities of the New Brunswick Laboratory for the period of October 1992 through September 1993.

LIST OF FREQUENTLY-USED ACRONYMS

ANL	-	Argonne National Laboratory	NMSS	-	Nuclear Materials Safety and Safeguards
ASTM	-	American Society for Testing and Materials	NA	-	Numerical Analysis
CTA	-	Central Training Academy	OpO	-	Operations Offices
CH	-	Chicago Operations Office, DOE	OR	-	Oak Ridge Operations Office, DOE
CRM	-	Certified Reference Material	ORNL	-	Oak Ridge National Laboratory
DOE	-	U. S. Department of Energy	ORR	-	Operational Readiness Review
HQ	-	Headquarters, DOE	OSS	-	Office of Safeguards and Security
HPT	-	High Precision Titration	PGDP	-	Paducah Gaseous Diffusion Plant
ICPP	-	Idaho Chemical Processing Plant	PORTS	-	Portsmouth Gaseous Diffusion Plant
ID	-	Idaho Operations Office, DOE	PuEx	-	Plutonium Metal and Isotopic Exchange Program
INMM	-	Institute of Nuclear Materials Management	QC	-	Quality Control
IRMM	-	Institute for Reference Materials and Measurements	RCRA	-	Resource Conservation and Recovery Act
LAN	-	Local Area Network	RD	-	Relative Difference
LANL	-	Los Alamos National Laboratory	RFO	-	Rocky Flats Office, DOE
LLNL	-	Lawrence Livermore National Laboratory	RFP	-	Rocky Flats Plant
MC&A	-	Material Control and Accountability	SCE	-	Saturated Calomel Electrode
MIP	-	Measurement Improvement Plan	SF	-	San Francisco (Oakland) Operations Office, DOE
MS	-	Mass Spectrometry	SME	-	Safeguards Measurement Evaluation
NBL	-	New Brunswick Laboratory	SNM	-	Special Nuclear Material
NDA	-	Nondestructive Assay	SRL	-	Savannah River Laboratory
NRC	-	U. S. Nuclear Regulatory Commission	SRS	-	Savannah River Site
			SSSP	-	Site Safeguards and Security Plan

EXECUTIVE SUMMARY

The New Brunswick Laboratory (NBL) fulfills its mission-related responsibilities by means of activities in the following programs: Safeguards Assistance, Measurement Evaluation, Measurement Development, Reference Materials, and Measurement Services. This annual report of accomplishments reflects a responsibility to transfer scientific technology to potential users in the safeguards community. Details of completed Development, Reference Material, or Evaluation projects are reported in separate topical reports or as open-literature publications.

Safeguards Assistance

NBL personnel provided safeguards assistance to Headquarters (HQ), to Operations Offices (OpO), and to contractor facilities as requested by their Operations Offices to meet the Laboratory's mission requirements. During FY 93 twelve NBL personnel participated in eleven periodic surveys with seven (AL, ID, OR, RF, SF, SR, and CH) different Operations Offices. The NBL assistance to Material Control and Accountability (MC&A) survey teams included materials control reviews on four of the eleven surveys conducted. Assistance to HQ for MC&A expertise in FY 93 included work for SA-12, SA-13, DP-68, EM-15, and NE. Assistance to SA-12 involved writing and reviewing of policy documentation; HQ/Germantown on-site assistance was provided for 6 months and reviews were done at NBL for SA-13. On-site reviews performed for HQ included two on-site readiness reviews at Rocky Flats and Savannah River for DP-68, one transition review at Rocky Flats for EM-15, and one Safeguards and Security Division review at Idaho for NE. Assistance to the Central Training Academy (CTA) for development and review of three MC&A courses occurred during FY 93. One training class on mass spectrometry for Paducah Gaseous Diffusion Plant (GDP) was held at NBL. NBL completed site-specific assistance activities with the Paducah GDP and the Idaho Chemical Processing Plant (ICPP). One general assistance activity for developing materials for safeguards performance testing is also being done as a coordinated effort between the Safeguards Assistance Program and the Measurement Evaluation Program.

Measurement Evaluation

NBL provided technical support to DOE/OSS by independently evaluating the adequacy of measurement technology as applied to materials accounting in DOE nuclear facilities. This support is provided both through operation of the NBL Safeguards Measurement Evaluation (SME) Program, which monitors the quality of uranium accountability destructive analyses, and through collaboration with contractor-operated evaluation programs. This fiscal year, NBL has begun efforts to reactivate a plutonium inter-laboratory destructive measurement evaluation program (Plutonium Exchange Program-PuEx).

The NBL SME Program was developed as a means to monitor and evaluate the quality and effectiveness of accounting 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. Resulting data are statistically evaluated, and a report is issued to the contractor and cognizant DOE Operations Office. Utilizing information included in the recently-issued DOE/OSS Measurement Control Guide and Measurement Improvement Plan, SME Program reports this year have begun to include an evaluation as to whether or not the reporting facilities have achieved accuracy and precision within the appropriate target values.

Measurement Development

Development Program activities focused on activities in the areas of staff technical training, upgrades to existing instrumentation, method improvements to existing techniques, investigations of current techniques, and installation and testing of analytical instrumentation.

A radiochemistry training course was started for the technical staff at the laboratory. The "Radiochemistry" course, based on the American Chemical Society audio training program, is being taught by the technical staff at the Laboratory and will be completed in FY 94. Five seminars were also held this year at NBL for the technical staff.

As part of sample preparation for mass spectrometric analysis, NBL tested purification of samples using ion-exchange columns. These tests were designed to qualify the ion-exchange technique using U/TEVA-Spec™ columns by comparing the isotopic results obtained on uranium samples using this method to those obtained by the currently used and qualified method of ether extraction. The U/TEVA-Spec™ method is being statistically evaluated for routine use and could result in obtaining more pure and more predictable concentrations of uranium for isotopic analysis.

A uranium blind standards program was developed for the NBL High Precision Titrimetric Method as part of the Quality Assurance Program at the laboratory. The program consisted of the design, preparation, and "blinding" of traceable uranium standards. These blinded standards were then used in a statistical design study to establish quality control limits for the NBL High Precision Titrimetric Method.

NBL tested an alternate procedure for the NBL-Modified Davies and Gray Titrimetric Method. In this approach, the non-RCRA-listed ceric ion was used as the oxidant to replace the RCRA-listed dichromate. Results from preliminary titrations indicate that the method using Ce(IV) as a titrant is promising. Additional tests and a statistical evaluation are in progress to qualify this new method.

The third generation NBL Controlled-Potential Coulometer system has been upgraded by replacing the HP9000-Model Computer with a HP PC-313CM BASIS controller on a HP Vectra 386/20 computer. The upgrade included software enhancements and testing the operational performance of the new system.

A Chemchek Kinetic Phosphorescence Analyzer has been purchased, set-up and tested for the determination of ng/L (ppt) to mg/L (ppm) concentrations of uranium in samples. Initial results indicate that the method has better accuracy and precision than those obtained by the fluorometric determination of uranium. The method is being statistically evaluated for use in routine low level uranium analyses at the Laboratory.

A VG Instruments inductively coupled plasma mass spectrometer has been installed in one of the plutonium laboratories. The instrument has passed all acceptance tests. Additional modifications and testing will be required before radioactive materials can be analyzed. The instrument has ng/g (ppb) sensitivity and will support NBL's capabilities for trace elemental analysis in nuclear materials.

A Finnigan MAT281 UF_6 mass spectrometer has been installed for reference material certification and sample analyses at the laboratory. Specification tests and sample test measurements have to be completed prior to the use of the instrument for uranium isotopic analysis.

The gamma-ray spectrometric evaluation of the European Community's Central Bureau of Nuclear Measurement (now the Institute for Reference Materials and Measurements--IRMM) pilot reference materials has lead to the determination of precise plutonium gamma-ray branching ratio values. The results will be published next year.

A spreadsheet detailing the complete radioactive decay scheme of actinide radioactive samples of interest was developed at NBL. With the input of mass and isotopic composition of the material at a given time, the program calculates the mass and activity of all daughters at a specified time. The program finds use in predicting the composition of a sample at any given time for the safe handling and shipping of nuclear materials as required by safety and transportation regulations.

All testings have been completed on a computer program, that has been developed at the NBL, for calculating the isotopic abundance of uranium and plutonium samples from gamma spectrometric measurements. This program has applicability to uranium and plutonium sample measurement and verification activities at the Laboratory.

A paper titled "Non-Destructive Assay techniques at New Brunswick Laboratory," was presented by Dave Baran at the Industrial & Nuclear Sensors and Systems, Inc., semi-annual seminar series held in April at Los Angeles. A paper titled "Process Waste Assessment at NBL" was presented by Usha Narayanan at the Waste Minimization and Pollution Prevention Conference IX held in April at San Francisco. NBL also prepared and submitted Waste Minimization Project proposals to the Director, Waste Minimization Division, EM-352 and to the Office of Strategic Environmental Research and Development Program.

Reference Materials

A primary responsibility of NBL to the DOE Safeguards Program is to provide nuclear reference materials to insure that safeguards measurements meet essential compatibility, reliability, and traceability to the national measurement base as mandated by DOE. During FY 93, 59 different certified reference materials (CRMs) were available for sale. Of these, 42 CRMs had sales ranging from 1 to 112 units. Purchasers of CRMs represented 48 separate organizations including 7 U. S. DOE contractors, 14 U. S. Nuclear Regulatory Commission (NRC) licensees, 7 U. S. academic institutions, 5 other U. S. customers, and 15 facilities in 15 foreign countries. NBL filled a total of 88 orders (33 foreign and 55 domestic) for 538 units (318 foreign and 220 domestic) valued at \$171,625.

Measurement Services

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 an arm of OSS and provides services on a contractual basis to NRC. During FY 93, NBL received 112 uranium samples for analysis. A wide variety of analyses, such as titrimetry, gamma spectrometry, and mass spectrometry was performed on these samples.

NBL provided assistance to the DOE Anomaly Resolution Team (DART) by analyzing 19 uranium samples. These samples were dissolved, analyzed and reported in the shortest time period ever accomplished at NBL for a group of samples of this type. The average measurement uncertainty on the uranium assays was calculated to be better than 0.02% RSD and better than 0.003% RSD for the isotopic analyses. NBL also provided assistance to Y-12 by analyzing six uranyl nitrate solution samples to resolve a shipper/receiver difference and to the ICPP by characterizing three UO_3 working standards.

The NRC Office of Nuclear Materials Safety and Safeguards (NRC/NMSS) submitted a total of 61 uranium samples for materials verification under the Nuclear Materials Safeguards Program. These samples included pure product materials such as UO_2 powders and pellets, complex fuel materials, impure materials such as grinder sludges, incinerator and calcined ashes, and liquid samples such as uranyl nitrate solutions and discard tank samples.

The NRC contract with NBL, administered under the Measurement Services Program, also provides technical support and assistance. NBL provided technical support to the NRC Physical Security MC&A Licensing Inspection Section by assisting NRC inspectors during inspections at General Electric (GE) in Wilmington, NC (March, 1993), Babcock and Wilcox (B&W) in Lynchburg, VA (May, 1993), Siemens Nuclear Power Corporation (July, 1993), and Westinghouse CFFF (September, 1993). NBL helped evaluate the effectiveness of the licensees' special nuclear material measurement systems and control programs to verify compliance with 10 CFR 74.31, 74.51, or 75.1, and helped collect samples for inventory verification.

SAFEGUARDS ASSISTANCE PROGRAM

W. G. Mitchell

Summary

NBL personnel provided safeguards assistance to Headquarters (HQ), to Operations Offices (OpO), and to contractor facilities as requested by their Operations Offices to meet the Laboratory's mission requirements. During FY 93 twelve NBL personnel participated in eleven periodic surveys with seven (AL, ID, OR, RF, SF, SR, and CH) different Operations Offices. The NBL assistance to Material Control and Accountability (MC&A) survey teams included materials control reviews on four of the eleven surveys conducted. Assistance to HQ for MC&A expertise in FY 93 included work for SA-12, SA-13, DP-68, EM-15, and NE. Assistance to SA-12 involved writing and reviewing of policy documentation; HQ/Germantown on-site assistance was provided for 6 months and reviews were done at NBL for SA-13. On-site reviews performed for HQ included two on-site readiness reviews at Rocky Flats and Savannah River for DP-68, one transition review at Rocky Flats for EM-15, and one Safeguards and Security Division review at Idaho for NE. Assistance to the Central Training Academy (CTA) for development and review of three MC&A courses occurred during FY 93. One training class on mass spectrometry for Paducah Gaseous Diffusion Plant (GDP) was held at NBL. NBL completed site specific assistance activities with the Paducah GDP and the Idaho Chemical Processing Plant (ICPP). One general assistance activity for developing materials for safeguards performance testing is also being done as a coordinated effort between the Safeguards Assistance Program and the Measurement Evaluation Program.

Operations Office Periodic Survey Assistance

NBL personnel performed periodic survey assistance to the Operations Offices for SA-13, the Office of Safeguards and Security's (OSS) Field Operations Division. Notification of assistance to OpO for MC&A subteams for surveys has been made to SA-13 throughout the year. NBL provides assistance as specified by the OpO in the areas of material accountability, measurement and measurement control, and material control.

Two NBL personnel assisted in the OR survey at Oak Ridge National Laboratory (ORNL) the week of October 26-30, 1992; the final report from NBL on the OR/ORNL survey was sent to OR in November. Three NBL personnel participated in the ID survey at ICPP the week of November 2-6, 1992; the final NBL report on the ID/ICPP survey was completed and sent with the work papers in January. Two NBL personnel participated in the OR/Paducah GDP survey of November 30-December 4, 1992; the final NBL report was written and sent to OR in December. One person participated in the Sandia/Livermore survey December 1-4, 1992; a report was prepared at the site. One person participated in the Sandia/Albuquerque survey February 16-26, 1993; a report was prepared at the site. Two persons participated in the SF/Lawrence Livermore National Laboratory survey of March 8-19, 1993; the final report was prepared before leaving the site. Two persons participated in the RFO survey of the Rocky Flats Plant from April 12-23, 1993; a classified report was prepared at the site. One NBL person participated in the CH survey of

Argonne National Laboratory-West (ANL-W) from April 26-May 5, 1993; a completed report was sent to CH in May. Two NBL personnel participated in the OR survey of the Y-12 Plant from June 6-18, 1993; a report was issued to OR in July. One NBL person participated in the Albuquerque Operations Office (AL) survey of the Los Alamos National Laboratory (LANL) of June 21-July 2, 1993; a report was prepared at the site. Two NBL personnel participated in a review of the analytical laboratory at Savannah River for the SR in July 12-16, 1993; a report was sent to SR in August. Three personnel from NBL participated in the periodic survey performed by OR of the Portsmouth GDP from September 20-October 1, 1993; a report was provided to OR in October as requested.

To meet Operations Offices' requests for broader NBL participation in material control and accountability surveys, NBL has participated in review of material control when requested. The NBL assistance to MC&A survey teams included materials control reviews on four of the eleven surveys conducted in FY 93. The CTA class, "Basics of Material Control" (MCA-120) was taught at NBL in September 1993 to 17 NBL employees to aid in broadening response to this stated need.

NBL personnel provided performance testing for accountability measurements on three Safeguards and Security surveys as requested by Operations Offices in FY 93. These performance tests may use materials provided in the cooperative effort with the NBL Safeguards Measurement Evaluation Program.

NBL Assistance to Headquarters

As part of its mission, NBL provides review and comment on MC&A policy documents as requested by SA-124. NBL provided information for the annual MC&A review by OSS which includes the common MC&A deficiencies identified in FY 93 surveys. The deficiencies are as follows:

1. Missing or out of date analysis procedures for accountability measurements were noted in 8 of the 11 surveys.
2. Inadequate training or incomplete documentation of training for personnel performing accountability measurements were noted in 4 of 11 surveys. Inadequate training or documentation of training of nuclear material control personnel were noted in two surveys.
3. Missing or poorly documented measurement control programs for accountability measurement methods were found in 6 of 11 MC&A surveys.
4. Use of an insufficient number of calibration standards or use of reference standards not traceable to the national measurement base for calibration was noted in three surveys.
5. Other deficiencies found in the surveys included: a) poor coordination of emergency planning with material control before reentry into a material access area, b) poor coordination between security and

MC&A for vulnerability analysis, and c) poor communications between quality control personnel for measurements and MC&A personnel.

NBL had personnel in residence at OSS/Germantown for over half of FY 93 to provide on-site MC&A expertise. OSS funding of safeguards related research and development was a primary area of assistance at OSS/Germantown. NBL also did 17 Small Business Innovative Research (SBIR) reviews at NBL for OSS related to funding of safeguards research and development. All of the SBIR reviews were on technology related to nuclear materials measurement or control; nine were on nondestructive assay, three were on material inventory systems, two were on material tagging, two were on material storage containers, and one was a destructive assay measurement system.

A DOE Anomaly Resolution Team (DART) Plan with a Workbook for application to material control and accountability was completed in FY 93 for SA-13. The plan will be issued by OSS upon final approval. The first DART was lead by NBL in April 1993. Samples to aid in the resolution of the shipper/receiver difference of the DART were analyzed at NBL.

The NBL provided MC&A expertise to other HQ offices at the request of OSS including two on-site readiness reviews at Rocky Flats and Savannah River for DP-68, one transition review at Rocky Flats for EM-15, and one Safeguards and Security Division review at Idaho for NE. Reports were provided at the site for each of the reviews.

Direct Central Training Academy Assistance

MC&A training in measurement and measurement control has been a major NBL effort in FY 93. NBL participated in the Training Working Group at the CTA at the request of OSS. NBL personnel prepared and taught modules in MCA-130, "Statistical Concepts in MC&A;" MCA-120, "Basics of Material Control;" MCA-140, "Basic Measurements for MC&A;" and MCA-142, "Volume Measurements Technique." Another CTA course for which NBL prepared a teaching module is ISC-221, "Classified Matter Protection and Control."

Site-Specific Assistance

At the request of the Operations Office, NBL will assist the sites in meeting analysis needs to improve the safeguards measurement posture of the site.

NBL participated in site specific assistance to Paducah Gaseous Diffusion Plant (PGDP) for verification measurements on UF₆ enriched uranium standards for traceability to the national measurements base. A protocol for the sample analyses was defined through the cooperation of NBL and PGDP's statistical

personnel. A series of measurements was performed on the PGDP materials, a statistical evaluation of the data was performed, and a report to the Operations Office and site was written.

NBL provided assistance to the ICPP for traceability of active-well coincidence counter standards being prepared for ICPP by Y-12. Samples from the standards were analyzed (assay and isotopic) by NBL, a statistical evaluation on the assay and isotopic results was provided, and the results were reported to the Idaho Operations Office and ICPP.

Publications

A white paper provided by the NBL on the coalescing of small plutonium (Pu) metal samples into larger, more attractive forms was distributed by OSS in FY 93 to those sites requesting guidance information on rollup concerns of small Pu metal pieces.

A paper, "Performance Testing Accountability Measurements," on NBL's performance testing capabilities for surveys was presented at the July 1993 Institute of Nuclear Materials Management meeting. NBL reviewed and evaluated the Central Training Academy's (CTA) class, "Introduction to Performance Testing" (MCA-103) in June 1993.

The OSS survey of DOE measurement technologies, applications, and random and systematic errors was issued to the field in May 1993. The Measurement Improvement Plan (MIP), written in FY 92 as a guide to DOE Operations Office and facility personnel, was distributed by OSS in June 1993. The MIP contains bibliographies on measurement methods and the international target values for nuclear material measurements.

PERFORMANCE TESTING ACCOUNTABILITY MEASUREMENTS

R. D. Oldham, W. G. Mitchell, and M. I. Spaletto

NBL has been involved in performance testing of accountability measurement systems long before this became a requirement in DOE Order 5633.3A. During MC&A Surveys, DOE Operations Office personnel collected and submitted inventory verification samples to NBL. The comparison and evaluation of the results obtained by NBL to the values obtained by the contractor on splits of the same samples was a direct indication of the capability of the contractor to perform measurements on real inventory items. With the increased involvement of NBL in assessment activities, requests have been received from DOE Operations Offices (primarily DOE-Oak Ridge) for NBL to design and assist with accountability measurement performance tests at contractor facilities. NBL is uniquely qualified to provide this assistance since it is an

independent, Government-Owned, Government-Operated (GOGO) standards laboratory that has the capability to prepare and characterize the test materials, the measurements personnel with the technical expertise necessary to evaluate the measurement systems, and the statisticians necessary to evaluate the performance test data.

To meet these requests, NBL has developed measurement and measurement control performance test procedures and materials. The present NBL repertoire of performance tests includes the following: 1) mass measurement performance tests using calibrated and traceable test weights, 2) uranium elemental concentration (assay) measurement performance tests using ampulated solutions of normal uranyl nitrate containing approximately 7 milligrams of uranium per gram of solution, and 3) uranium isotopic measurement performance tests using ampulated uranyl nitrate solutions with enrichments ranging from 4% to 90% ^{235}U . The preparation, characterization, and packaging of the uranium isotopic and assay performance test materials were done in cooperation with the NBL Safeguards Measurements Evaluation Program since these materials can be used for both purposes.

During the past year, there have been significant improvements to the NBL performance tests. Documentation has been improved and the performance tests now meet the requirements of DOE Order 5630.16A on Performance Testing. The performance test plans have also been made generic and with only slight modification can be applied to any uranium assay, uranium isotopic, or mass measurement system. In addition, a graded approach is now used to select the measurement systems or methods for evaluation. Selection is based on the critical nature of the accountability measurements which are being performed on the measurement systems. Primary consideration is given to the testing of measurement systems which have been identified in Vulnerability Assessments (VAs) as making critical measurements. High priority is given to measurement systems which measure the major material flows or large inventories. Finally, these performance test plans also evaluate if the measurements and measurement control requirements of DOE Order 5633.3A are being met. The tests evaluate the selection and qualification of the measurement method, the maintenance and calibration program (including traceability), the training and qualification of the measurement personnel, and the measurement control program.

Since measurements performance testing is now required by DOE Orders, it is anticipated that NBL will receive additional requests from DOE Operations Offices for assistance with measurements performance tests in the future. NBL is prepared to meet these requests. This assistance may either involve the direct participation of NBL personnel during the performance test or the supplying of test materials and performance test plans for use by the Operations Office.

As indicated earlier, a properly designed and documented plan for independent verification measurements on a portion of the inventory can also be a performance test. The comparison and evaluation of the results obtained by NBL to those of the contractor on sample splits is a direct indication of the capability of the contractor to perform assay or isotopic measurements on real inventory items. It is planned to develop a generic performance test plan for inventory verification measurements during FY 94 which can be used by NBL assistance teams or DOE Operations Office personnel during MC&A surveys at contractor facilities.

PADUCAH UF₆ WORKING STANDARDS

V. E. Connolly, M. M. Smith, and W. G. Mitchell

In support of DOE/OSS, NBL provides assistance to site contractors at the request of the cognizant Operations Offices. Operations Offices, working with their contractors, identify areas for which NBL assistance may be appropriate. One area of assistance involves a priority for analysis of needed measurement control standards which may temporarily exceed the contractors' analytical facility capacity. The Operations Office may request assistance from NBL, the DOE Safeguards Laboratory, in meeting safeguards requirements for identified deficiencies.

The Paducah Gaseous Diffusion Plant (PGDP) uses UF₆ gas mass spectrometry as an accountability measurement for their cascade, a potentially major measurement contributor to any inventory difference. The working reference materials were purchased from the National Institute of Standards and Technology (formerly the National Bureau of Standards) in 1964; the material was not a Standard or Certified Reference Material (SRM or CRM). This material was analyzed internally and in a round-robin study to determine reference values but had no traceability to a national measurement base. A recommendation was made by the OR to establish such traceability.

The NBL agreed to perform isotopic abundance measurements on the three PGDP UF₆ working reference materials in order to provide traceability to a national or international measurement base. Since NBL currently does not have a gaseous UF₆ measurement capability, PGDP converted four portions of each of the three working reference materials to U₃O₈ and shipped them to NBL for thermal ionization mass spectrometric isotopic abundance measurements, principally ²³⁵U.

At NBL, a measurement plan was developed which included the following elements:

1. Three 5-mg subsamples were taken from three of the four portions of each working reference material. These subsamples were dissolved and prepared for isotopic measurements according to the requirements of the measurement procedure.

2. Three reference materials from the CRM 969 series (a certified reference material series of ^{235}U enrichments for nondestructive assay) were selected as the most appropriate control standards for this project. [Although NBL has a small amount of this material retained from the original characterization measurements, these materials are not available for purchase for destructive analysis.]
3. An analysis plan with a schedule of subsample and quality control measurements was generated by the numerical analysis group. After completion of all the measurements, the data were statistically evaluated.

The subsamples were dissolved and diluted to a concentration of 1 mg U/g in 0.8N nitric acid (HNO_3) as required for measurements with the Finnigan MAT261 uranium isotopic procedure (NBL-SA-U(I)-4)¹. Calibration measurements with CRM U500 were performed to determine the mass correction factor. Measurements with other CRMs were performed to assure a linear response of the measurement system; measurements on the control standards were included. The analysis plan specified thirty-nine measurements, three turrets of thirteen measurements on each turret using the fully automated mode of operation. Observations of the measurement performance for the first two turrets were consistent, but different than for the calibration measurements run with them. A new calibration turret with replicate CRM U500 loadings and loadings of the control standards was run next. This turret ran like the two sample turrets, and the results on the control standards agreed; however, the mass correction factor changed. The last of the three scheduled turrets was then loaded and this turret ran acceptably.

A spreadsheet with all the data, including the standard calibration, was created, and the information was submitted for statistical review. The only observation by the statistician was that there appeared to be some sample to sample variation on the PGDP 0.71% ^{235}U material. For two of the three samples of 0.71% ^{235}U material, there was an exceptionally small standard deviation on the subsample measurements. The standard deviation for the third 0.71% ^{235}U sample, and overall for the three samples of this material, was well within acceptable limits. Uncertainties for the PGDP UF_6 standard reference materials are expressed as the 95% confidence interval (CI). The $^{236}\text{U}/^{235}\text{U}$ ratios for the 0.71% ^{235}U material and CRM 969-071 were zeroed out, and the ^{236}U percentages were stated as a less than value after a statistical determination that the measured mean was not a significant value. The data are summarized in Table I.

REFERENCE

1. "Determination of Isotopic Composition of Uranium by Thermal Ionization Mass Spectrometry (MAT261)," NBL-SA-U(I)-4, NBL Procedures Manual, September 3, 1991.

TABLE I
SUMMARY: NBL VERIFICATION DATA - PADUCAH UF₆ WORKING REFERENCE MATERIALS

Standard/ Reference Material	Values	Uranium Isotopes			
		234	235	236	238
CRM 969-031 Certificate	Atom % Weight % Uncertainty $\pm$	0.0020 0.0020 0.0002	0.3206 0.3166 0.0002	0.0147 0.0146 0.0003	99.6627 99.6668 0.0004
CRM 969-031 Measured n=4	Atom % Weight % 95 % C.I. $\pm$	0.00197 0.00193 0.00016	0.32056 0.31652 0.00016	0.01492 0.01480 0.00051	99.66255 99.66674 0.00057
PGDP 0.14 Measured n=9	Atom % Weight % 95 % C.I. $\pm$	0.00041 0.00040 0.00016	0.14578 0.14395 0.00010	0.00335 0.00332 0.00022	99.85046 99.85233 0.00024
CRM 969-071 Certificate	Atom % Weight % Uncertainty $\pm$	0.0053 0.0052 0.0002	0.7209 0.7119 0.0005	<0.00002 <0.00002	99.2738 99.2828 0.0004
CRM 969-071 Measured n=5	Atom % Weight % Uncertainty $\pm$	0.00513 0.00504 0.00014	0.72051 0.71148 0.00042	<0.0001 <0.0001	99.27436 99.28348 0.00050
PGDP 0.71 Measured n=9	Atom % Weight % 95 % C.I. $\pm$	0.00546 0.00537 0.00015	0.72012 0.71108 0.00038	<0.0001 <0.0001	99.27443 99.28356 0.00036
CRM 969-446 Certificate	Atom % Weight % Uncertainty $\pm$	0.0365 0.0359 0.0003	4.5168 4.4623 0.0032	0.0069 0.0068 0.0002	95.4398 95.4950 0.0032
CRM 969-446 Measured n=4	Atom % Weight % 95 % C.I. $\pm$	0.03691 0.03631 0.00032	4.5169 4.4625 0.0020	0.00685 0.00680 0.00022	95.4393 95.4944 0.0021
PGDP 4.46 Measured n=9	Atom % Weight % 95 % C.I. $\pm$	0.03862 0.03799 0.00012	4.5158 4.4613 0.0015	0.02763 0.02741 0.00015	95.4180 95.4733 0.0015

Note: CRM 969 is a set of five NDA standards in sealed containers and is not generally available for mass spectrometric abundance measurements. This NBL material was used because it was the best available match of two of the materials to the UF₆ working reference materials.

IDAHO CHEMICAL PROCESSING PLANT (ICPP) WORKING STANDARDS

A. V. Stiffin, I. W. Frank, and V. E. Connolly

NBL provided assistance to the ICPP at the request of ID by characterizing three UO_3 working standards. These standards were fabricated by Martin-Marietta at Y-12 in Oak Ridge, Tennessee, for ICPP use as Active-Well Coincidence Counter working standards. The samples from the standards were received in May, 1993, and the assay results were reported in August, 1993. The analyses consisted of the determination of the uranium content using the NBL Modified Davies and Gray Titration method and the determination of the uranium isotopic composition using thermal ionization mass spectrometry.

A statistical design of experiment was requested prior to starting the sample analyses. The design required the taking of eight (8) aliquants from each of the three sample solutions. Three aliquants of each of the three solutions would be titrated, and the data would be submitted to the statistician at NBL. If no statistically significant sample-to-sample variation were to be detected, the results would be reported with no more analyses being performed. If sample-to-sample variation were to be detected, the five (5) additional analyses on each sample would be required as each sample would then be characterized individually. Also, three aliquants of each sample solution were submitted for isotopic analysis. If significant variation were to be found for the titration samples, two more isotopic analyses per sample solution would be performed.

The results of the titrimetric analyses showed no statistically significant variations so no further work was needed on either the uranium determinations or the isotopic determinations. The results of the uranium titration analyses are shown in Table I. The NBL statistician analyzed the titration data and concluded that there was only marginal evidence of sample-to-sample variation even with the statistical outlier included. All nine results were reported to ICPP and ID.

Three to four mass spectrometric analyses were done on each of the samples of the three standards. Statistical tests confirmed that there were no outlying values in the data set and that there were no sample-to-sample variations in the isotopic values. Three results for samples 93EU0064 and 93EU0065 were reported; four results for 93EU0066 were reported. The mean weight percent values of the mass spectrometry analyses are listed in Table II.

TABLE I		
INDIVIDUAL AND SUMMARY URANIUM ASSAY RESULTS ON ICPP STANDARDS		
NBL No.	Allquant No.	gU/g sample
93EU0064	000-005	0.827239
93EU0064	000-006	0.827419
93EU0064	000-007	0.827239
93EU0065	000-002	0.827172
93EU0065	000-003	0.827268
93EU0065	000-006	0.827334
93EU0066	000-006	0.827511
93EU0066	000-007	0.827819*
93EU0066	000-008	0.827383
	Mean	0.82738
	Std. Dev.	0.00020
	95% C.I.	± 0.00015

* Statistical Outlier

TABLE II					
MEAN WEIGHT % VALUES FOR ISOTOPIC DATA ON ICPP STANDARDS					
Isotope	Mean, Wt%	Standard Deviation	N	95% C.I. ¹	Analyst Estimate ²
²³⁴ U	1.01506	0.00054	10	± 0.00039	± 0.00100
²³⁵ U	93.15717	0.00278	10	± 0.00199	± 0.00500
²³⁶ U	0.44272	0.00030	10	± 0.00022	± 0.00050
²³⁸ U	5.38508	0.00312	10	± 0.00223	± 0.00500

Statistician's Notes:

¹ This column contains an estimate of uncertainty based solely on random error.

² This column contains the analyst's estimate of uncertainty based on both random and systematic error.

MEASUREMENT EVALUATION PROGRAM

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

Safeguards Measurement Evaluation Program Information

NBL provides technical support to DOE/OSS by independently evaluating the adequacy of measurement technology as applied to materials accounting in DOE nuclear facilities. This support is provided both through operation of the NBL Safeguards Measurement Evaluation (SME) Program, which monitors the quality of uranium accountability destructive analyses, and through collaboration with contractor-operated evaluation programs. This fiscal year, NBL has begun efforts to reactivate a plutonium Inter-laboratory destructive measurement evaluation program (Plutonium Exchange Program-PuEx).

The NBL SME Program was developed as a means to monitor and evaluate the quality and effectiveness of accounting 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. Resulting data are statistically evaluated, and a report is issued to the contractor and cognizant DOE Operations Office. Utilizing information included in the recently-issued DOE/OSS Measurement Control Guide and Measurement Improvement Plan, SME Program reports this year have begun to include an evaluation as to whether or not the reporting facilities have achieved accuracy and precision within the appropriate target values.

Normal Uranyl Nitrate Material

In fiscal year 1992, a suite of three normal uranyl nitrate solutions was characterized for uranium concentration and distributed for analysis. These solutions enable the participation of facilities restricted from receiving shipments of enriched materials. The elemental assay of each solution differs from the next by approximately 0.1%. The ability to differentiate these materials demonstrates good analytical capabilities. Paducah Gaseous Diffusion Plant (GDP), Portsmouth GDP, NBL, and 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. During this reporting period, results were received for 38 samples of normal solutions. Twelve final reports, representing a total of 188 individual analyses, were issued to the facilities and cognizant Operations Offices through September, 1993. Analyst-to-analyst differences observed in the submitted data assisted in evaluating analyst training; observed day-to-day differences assisted in identifying instrument problems.

Los Alamos National Laboratory (LANL) has agreed to participate in this portion of the Program beginning next fiscal year. Because of the increased usage of these materials, plans for FY 94 include replacement of this suite of normal uranyl nitrate solutions.

Enriched Uranyl Nitrate Material

This fiscal year, the Program has added uranyl nitrate solutions intended for isotopic analysis. A solution of 50% enriched uranyl nitrate was characterized for isotopic distribution. The Program also has available for distribution three high-enriched (approximately 90% ^{235}U) uranyl nitrate solutions, and a low-enriched (approximately 4% ^{235}U) solution. A request has been received for the addition of a 20% ^{235}U material in FY 94.

NBL and Y-12 Plant have agreed to begin isotopic analyses of the enriched uranyl nitrate isotopic solutions. One report, representing a total of two analyses on two samples, has been issued.

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 in MC&A inspections. In the last fiscal year, these solutions were used at both Portsmouth GDP and Y-12 Plant for performance tests of elemental assay analysis.

Uranium Oxide Material

Uranium oxide (UO_3) is included in the SME Program to evaluate shipper-receiver measurements on hygroscopic uranium materials. Participants include NBL and the Y-12 Plant. During this reporting period, NBL distributed sixteen samples of UO_3 to participating facilities for analysis. Nine final reports, representing a total of 71 individual analyses, were issued to the facilities and cognizant Operations Offices through September, 1993.

Repackaging and recharacterization of this material began this fiscal year. Because the material is hygroscopic, it is vital to utilize containers that will prevent moisture uptake. Extensive testing of candidate containers has resulted in the selection of pharmaceutical serum bottles. The material will be dried, blended, packaged in the serum bottles in a drybox, and characterized in FY 94.

Uranium Hexafluoride Material

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. P-10 tubes of UF_6 were filled at NBL and distributed to NBL, Paducah GDP, and Portsmouth GDP. Ten reports, representing a total of 22 individual analyses, have been received and issued to these facilities and their Operations Offices.

Paducah GDP, Portsmouth GDP, and NBL are participating in the analysis of uranium-contaminated alumina UF_6 trap material. Sixteen samples have been distributed to the participants, and seventeen final reports have been generated, representing a total of 104 individual analyses. One facility is analyzing this material by multiple methods, using the Program to evaluate which method is the least biased.

Plutonium Materials

When the SME Program was first instituted, plutonium materials were included, but shipment of plutonium became so difficult that these materials were eliminated. Because of the shipping problem and the curtailment of activities at Rocky Flats Plant, the Rocky Flats Plutonium Isotopic and Metal Sample Exchange Programs have also been inactive for several years. OSS has tasked the NBL with introducing plutonium isotopic and elemental concentration determinations into its SME Program again. The NBL has prepared three solutions of differing isotopic distributions from previously-characterized materials and has prepared them for shipment. Argonne National Laboratory-West, LANL, NBL, Rocky Flats Plant, Westinghouse Savannah River, and Westinghouse Hanford have agreed to participate. These isotopic materials will be distributed and analyzed quarterly, with two solution samples to be analyzed per quarter. A quick-turnaround report including only relative differences (RDs) will be returned to each facility submitting results; the RD report will be followed by quarterly and annual reports summarizing data from all participants.

Since the NBL can no longer handle the larger quantities of plutonium that would be involved in the preparation and shipment of samples to be analyzed for elemental concentration, LANL has been tasked to support this effort. Plutonium concentration values will be determined by analyses performed by NBL and LANL; NBL will provide the analysis plan and perform the statistical evaluation to set the reference values. Like the plan for isotopic analyses, each participating facility will analyze two plutonium concentration samples per quarter with individual RD reports to be followed by semiannual and annual reports from NBL.

Papers and Meetings

The Program Manager prepared a paper for presentation at the Central Region Chapter Meeting of the Institute of Nuclear Materials Management. She also participated in a meeting at NBL with representatives from the Institute for Reference Materials and Measurements of the Joint Research Center for the Commission of the European Communities. Potential areas of collaboration with the Regular European Interlaboratory Measurement Evaluation Program were discussed. Future plans for the Measurement Evaluation Program also include exploring the possibility of participation in the SME Program by Nuclear Regulatory Commission licensees on a cost-recovery basis.

EVALUATION OF AN AUTOMATED TITRATOR

L. D. Preston and M. M. Smith

A semi-automated version of the NBL-Modified Davies and Gray Titrimetric Method (NBL Titrimetric Method) was developed.^{1,2} Validation results were reported in last year's annual report.³ In FY 93 an error was discovered in the calculations section of the new assay procedure. Results of the validation study were corrected accordingly.

Two sets of assays were dropped from statistical analysis because opening and closing "blind" measurement control standards exhibited an unacceptably high bias; even in assay of unknown samples an analyst would recognize that the titration system was not in control. To offset the loss of data, extra analyses performed during other Day/Analyst combinations were placed back into the data set. The results of the new statistical evaluation are given in Table I.

Sample aliquants were assayed with a mean RD of 0.011% (sd = 0.044%, n = 66); "blind" standards were assayed with a mean RD of -0.006% (sd = 0.044%, n = 26). Day-to-day variability was found to be statistically significant in sample assay but not in assay of measurement control "blinds"; analyst-to-analyst variability was only marginally significant for either "blinds" or samples. There was no statistically significant correlation between sample size (mg U) and bias. The new (95%) control limits for the method are $\pm 0.09\%$ RD.

TABLE I				
RESULTS OF STATISTICAL STUDY, BY DAY AND BY ANALYST				
	QC "Blind" Standards		Samples	
	n	$\bar{RD} \pm 95\% \text{ C.I.}$	n	$\bar{RD} \pm 95\% \text{ C.I.}$
Day 1	10	-0.0198 ± 0.0359	24	-0.0256 ± 0.0181
Day 2	10	$+0.0017 \pm 0.0306$	25	$+0.0346 \pm 0.0101$
Day 3	6	$+0.0028 \pm 0.0335$	17	$+0.0289 \pm 0.0169$
Analyst 1	7	$+0.0186 \pm 0.0512$	16	$+0.0149 \pm 0.0207$
Analyst 2	9	-0.0106 ± 0.0216	25	0.0177 ± 0.0183
Analyst 3	10	-0.0199 ± 0.0304	25	0.0025 ± 0.0193
Total	26	-0.0063 ± 0.0176	66	0.0112 ± 0.0108

The negative biases previously observed in assay of three SME uranyl nitrate solutions were found to be due to calculation errors. After correction, mean assay bias was -0.001% (sd = 0.021%, n = 15) for the uranyl nitrate solutions and 0.009% (sd = 0.035, n = 9) for "blind" standards. No solution-to-solution variations were evident. Results from the samples and the measurement control "blinds" were in agreement, as shown in Table II.

TABLE II			
RESULTS FOR SME URANYL NITRATE SAMPLES			
"Blinds"	Bottle 1	Bottle 2	Bottle 3
$\bar{RD} = +0.0087$ sd = 0.0355 n = 9	$\bar{RD} = +0.0074$ sd = 0.0092 n = 3	$\bar{RD} = -0.0071$ sd = 0.0236 n = 6	$\bar{RD} = +0.0009$ sd = 0.0235 n = 6

The semi-automated results are compared to results for "blinds" titrated manually by each chemist preceding the study in Table III.

TABLE III						
STUDY RESULTS COMPARED TO ANALYST QC DATA FOR MANUAL METHOD						
Analyst	Manual Method QC "Blinds"			Semi-Automated Method		
	n	$\bar{RD}$	RSD	QC "Blinds"	Study Samples	SME Samples
1	7	-0.0011	0.0192	$\bar{RD} = +0.0186$ RSD = 0.0553	$\bar{RD} = +0.0149$ RSD = 0.0389	N/A
	16	-0.0054	0.0293	n = 7	n = 16	
2	9	-0.0362	0.0262	$\bar{RD} = -0.0106$ RSD = 0.0280	$\bar{RD} = +0.0177$ RSD = 0.0443	N/A
	25	-0.0177	0.0417	n = 9	n = 25	
3	10	+0.0266	0.0374	$\bar{RD} = -0.0199$ RSD = 0.0426	$\bar{RD} = +0.0025$ RSD = 0.0467	N/A
	25	+0.0230	0.0309	n = 10	n = 25	
3	9	+0.0254	0.0395	$\bar{RD} = +0.0087$ RSD = 0.0355	N/A	$\bar{RD} = -0.0010$ RSD = 0.0210
	15	+0.0268	0.0308	n = 9		n = 15
3	19	+0.0230	0.0325	$\bar{RD} = -0.0063$ RSD = 0.0410	$\bar{RD} = +0.0012$ RSD = 0.0388	
	40	+0.0081	0.0407	n = 19	n = 40	

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ACQUISITION/EVALUATION OF A PYROHYDROLYSIS FURNACE

W. Nichiporuk and K. S. Scheidelman

The pyrohydrolysis furnace will enable NBL to obtain a gravimetric stoichiometry factor for the concentration of uranium in UF_6 samples converted to U_3O_8 by pyrohydrolysis. Other facilities have been using pyrohydrolysis furnaces for the gravimetric analysis of this material, and it is essential that NBL determine the stoichiometry factor in the same manner. The furnace was constructed in previous reporting periods¹, and has undergone extensive safety review during this fiscal year.

The pyrohydrolysis furnace safety checks, directed toward evaluating potential scalding hazards when steam is introduced into the system at its design flow rate of 1 kg/hr, were completed. No indication of any unsafe conditions were apparent when the steam valve operation instructions, developed by cooperative effort between the chemists and the Environment, Safety and Health Office, were habitually observed.

In addition, potential health hazards related to the flow of corrosive hydrogen fluoride and fluorine (HF and F_2) gases out of the vent hole on the front of the furnace during pyrohydrolysis of UO_2F_2 at 850°C were closely examined. Watch glass etching tests showed that a venting period of five minutes is fully sufficient for the evolved gases to clear the furnace chamber and safely escape into the fume hood.

With every Ignition run, a thermocouple connected to a calibrated digital thermometer was inserted in a position in the furnace corresponding to the center of a two-sample location area. This was being done because there invariably is a temperature gradient in the furnace in the presence of the swirling steam and HF and F_2 gases. However, even with this constant thermocouple positioning, the temperature control so far attained is no better than $850 \pm 10^\circ\text{C}$.

For a check of the furnace's performance, the contents of two P-10 tubes filled with UF_6 were hydrolyzed in cold water and evaporated to UO_2F_2 . These samples were then converted to U_3O_8 in the pyrohydrolysis furnace at 850°C , and taken to constant weight at the same temperature. Two U_3O_8 subsplits were taken from each pyrohydrolysis conversion for later evaluation by the NBL High-Precision Titrimetric Method and comparison with gravimetry.

A preliminary study will then compare gravimetry following conversion in a pyrohydrolysis furnace *versus* conversion in a furnace without superheated steam. This will be followed by a full-scale study in which

gravimetric results will also be compared to high-precision titrimetric results to determine the gravimetric factor experimentally. This factor, which is necessary for the conversion of gravimetric results to corresponding UF_6 elemental assay, is presently set by agreement between facilities.

REFERENCE

1. W. Nichiporuk, C. C. Marcelo, and K. S. Scheidelman, "Acquisition/Evaluation of a Pyrohydrolysis Furnace," NBL-327, pp. 21-22, 1993.

CHARACTERIZATION OF ISOTOPIC ABUNDANCES IN URANYL NITRATE SOLUTION: FIFTY PERCENT ^{235}U URANIUM

V. E. Connolly, A. J. Traina, M. D. Soriano, and M. I. Spaletto

As part of the Safeguards Measurement Evaluation (SME) Program, selected materials which are compatible with the needs of the participating facilities are prepared, characterized, and distributed by NBL for analysis on a periodic basis. NBL also provides each participant and the cognizant Operations Office with a report on the statistically-evaluated data for each material.

Uranyl nitrate solutions of various enrichment levels are needed in the program to evaluate site-specific isotopic abundance measurement performance. These materials may also be used in isotopic measurement and measurement control performance tests during DOE Operations Office surveys of contractor facilities.

Three high-enrichment solutions (90% ^{235}U) and one low-enrichment (4% ^{235}U) solution have previously been prepared and characterized. The characterization of a solution with a mid-level enrichment of approximately 50% ^{235}U was completed in the last two quarters of FY 93.

In FY 86, initial isotopic abundance measurements and uranium concentration determinations were made on six 50-mL ampules of the material; however, the primary focus of this work was on the uranium concentration values. In early FY 93, the contents of twelve of these ampules were pooled and re-ampulated into one hundred and forty 5-mL units. A measurement scheme for duplicate analysis of six ampules and appropriate controls was provided by the numerical analysis group. The six ampules to be analyzed were the first, last, and four other randomly selected units. The ampules were opened, the contents were evaporated to dryness in acid-leached 50 mL beakers, and were re-dissolved in 28 mL of 0.8N high purity nitric acid to a concentration of 1 mg U/g solution. Duplicate measurements were made on each ampule

using the U MAT261 mass spectrometer.¹ A total of twenty-two sample runs, including CRM U500 (to determine the mass correction factor) and CRM U750 (for quality control), were used for the characterization.

The data from this and the former characterization were incorporated into a spreadsheet, and the file was submitted for statistical review and evaluation. Data from the FY 93 isotopic measurements were compared to the FY 86 data and determined not to be significantly different. All data were then combined to provide the final reference values. After a preliminary review and discussion with the statistician, an equal-weighting scheme was selected for combining the two sets of data. The uncertainties for the measurements were well within the measurement capability of the instrument/method. There were two statistical notes of interest: 1) there was a small difference in the % ^{234}U between the two data sets of <0.0010 ; and 2) the % ^{236}U values for both standards were slightly high, but the difference was less than 0.0010. Absolute differences of this magnitude have very little impact on the sample % ^{236}U value, which is 100 to 200 times greater than that of the standards. The 238/235 ratios from the CRM U500 data were used to determine the mass correction factor. A small relative difference for the mean CRM U750 corrected 238/235 ratio (-0.0031% from the reference value) demonstrates the appropriateness of applying the mass correction factor to the other data. A summary of the results is given in Table I. Eighteen measurements (the original six and the duplicates of the second six ampules) were pooled, each as an independent value. The statistical uncertainties are expressed as the standard deviation of the mean (Std Error) and the 95% confidence interval (CI), the Std Error times a factor based on the statistical degrees of freedom (d.f.).

<p>TABLE I</p> <p>CHARACTERIZATION VALUES FOR 50% ^{236}U SME UNH SOLUTION</p> <p>ISOTOPIC ABUNDANCES</p>				
Value	^{234}U	^{235}U	^{238}U	^{236}U
Atom %	1.3023	51.5003	29.9722	17.2252
Std. Error	0.0002	0.0016	0.0009	0.0011
d.f.	7	10	5	16
95% CI	0.0004	0.0036	0.0024	0.0023
Weight %	1.2923	51.3245	29.9972	17.3860

A trace amount of ^{233}U ($\leq 0.0010\%$) was detected during both years' characterization efforts; this was not included in the abundance calculations. If the ^{233}U were included, the value for ^{235}U would be reduced by 0.0005; the value for ^{236}U would be reduced by 0.0003; and the value for ^{238}U would be reduced by 0.0002.

REFERENCE

1. "Determination of Isotopic Composition of Uranium by Thermal Ionization Mass Spectrometry (MAT261)," NBL-SA-U(I)-4, NBL Procedures Manual, September 3, 1991.

MEASUREMENT DEVELOPMENT PROGRAM

U. I. Narayanan

Development Program activities focused on activities in the areas of staff technical training, upgrades to existing instrumentation, method improvements to existing techniques, investigations of current techniques, and installation and testing of analytical instrumentation.

A radiochemistry training course was started for the technical staff at the laboratory. The "Radiochemistry" course, based on the American Chemical Society audio training program, is being taught by the technical staff at the Laboratory and will be completed in FY 94. Five seminars were also held this year at NBL for the technical staff.

As part of sample preparation for mass spectrometric analysis, NBL tested purification of samples using ion-exchange columns. These tests were designed to qualify the ion-exchange technique using U/TEVA-Spec™ columns by comparing the isotopic results obtained on uranium samples using this method to those obtained by the currently used and qualified method of ether extraction. The U/TEVA-Spec™ method is being statistically evaluated for routine use and could result in obtaining purer and more predictable concentrations of uranium for isotopic analysis.

A uranium blind standards program was developed for the NBL High Precision Titrimetric Method as part of the Quality Assurance Program at the laboratory. The program consisted of the design, preparation, and blinding of traceable uranium standards. These blinded standards were then used in a statistical design study to establish quality control limits for the NBL High Precision Titrimetric Method.

NBL tested an alternate procedure for the NBL-Modified Davies and Gray Titrimetric Method. In this approach, the non-RCRA listed ceric ion was used as the oxidant to replace the RCRA listed dichromate. Results from preliminary titrations indicate that the method using Ce(IV) as a titrant is promising. Additional tests and a statistical evaluation are in progress to qualify this new method.

The third generation NBL Controlled-Potential Coulometer system has been upgraded by replacing the HP9000-Model Computer with a HP PC-313CM BASIS controller on a HP Vectra 386/20 computer. The upgrade included software enhancements and testing the operational performance of the new system.

A Chemchek Kinetic Phosphorescence Analyzer has been purchased, set-up and tested for the determination of ng/L to mg/L concentrations of uranium in samples. Initial results indicate that the method has better accuracy and precision than those obtained by the fluorometric determination of uranium. The method is being statistically evaluated for use in routine low level uranium analyses at the Laboratory.

A VG Instruments inductively coupled plasma mass spectrometer has been installed in one of the plutonium laboratories. The instrument has passed all acceptance tests. Additional modifications and testing will be required before radioactive materials can be analyzed. The instrument has ng/g (ppb) sensitivity and will support NBL's capabilities for trace elemental analysis in nuclear materials.

A Finnigan MAT281 UF_6 mass spectrometer has been installed for reference material certification and sample analyses at the laboratory. Specification tests and sample test measurements have to be completed prior to the use of the instrument for uranium isotopic analysis.

The gamma-ray spectrometric evaluation of European Community's Central Bureau of Nuclear Measurement (now the Institute for Reference Materials and Measurements--IRMM) pilot reference materials has led to the determination of precise plutonium gamma-ray branching ratio values. The results will be published next year.

A spreadsheet detailing the complete radioactive scheme of actinide radioactive samples of interest was developed at NBL. With the input of mass and isotopic composition of the material at a given time, the program calculates the mass and activity of all daughters at a specified time. The program finds use in predicting the composition of a sample at any given time for the safe handling and shipping of nuclear materials as required by safety and transportation regulations.

All testings have been completed on a computer program, that has been developed at the NBL, for calculating the isotopic abundance of uranium and plutonium samples from gamma spectrometric measurements. This program has applicability to uranium and plutonium sample measurement and verification activities at the Laboratory.

A paper titled "Non-Destructive Assay techniques at New Brunswick Laboratory," was presented by Dave Baran at the Industrial & Nuclear Sensors and Systems, Inc., semi-annual seminar series held in April at Los Angeles. A paper titled "Process Waste Assessment at NBL" was presented by Usha Narayanan at the Waste Minimization and Pollution Prevention Conference IX held in April at San Francisco. NBL also prepared and submitted Waste Minimization Project proposals to the Director, Waste Minimization Division, EM-352 and to the office of Strategic Environmental Research and Development Program.

γ SPECTROMETRIC EVALUATIONS OF IRMM PILOT PLUTONIUM REFERENCE MATERIALS

D. T. Baran

A two-year project aimed at measuring the ^{241}Pu 148.567 keV-, the ^{238}Pu 152.680 keV-, the ^{241}Pu 159.955 keV-, and the ^{240}Pu 160.280 keV- γ -ray branching ratios has been completed. This report briefly summarizes the results. Details of the measurement procedure, instrumentation and calculations can be found elsewhere^{1,2}

Table I shows the results of the study. The results are based on the analysis of 16 spectra obtained from the measurement of the four IRMM (formerly CBNM) standards on 3 different detectors. The additional spectra and the utilization of three independent detector systems increased the statistical significance of the results by reducing the random error and any systematic errors associated with any one detector system.

TABLE I		
NBL RESULTS		
Energy (keV)	NBL	World Average³
148.567	$(1.863 \pm 0.008) \times 10^{-6}$	$(1.86 \pm 0.02) \times 10^{-6}$
152.680	$(9.230 \pm 0.068) \times 10^{-6}$	$(9.37 \pm 0.10) \times 10^{-6}$
159.955	$(6.321 \pm 0.040) \times 10^{-8}$	$(6.58 \pm 0.09) \times 10^{-8}$
160.280	$(4.065 \pm 0.017) \times 10^{-6}$	$(4.02 \pm 0.04) \times 10^{-6}$

The results in Table I are slightly different from those reported last year². The differences are primarily due to the inclusion of 12 additional analyzed spectra collected using the three different detector systems. In addition, a detailed study and estimation of systematic errors introduced through the seven parameter peak-fitting program was performed. The study resulted in a reduction of the overall error in the peak-fitting process. Finally, an independent verification of the data analysis spreadsheets, validating numeric results⁴ was accomplished. The final results for the branching ratios reported here suggest that it may be necessary to revise the world-wide accepted values of at least two of the four branching ratios.

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DEVELOPMENT OF A COMPUTERIZED SYSTEM FOR THE ISOTOPIC ANALYSIS OF SOLIDS

D. T. Baran

Introduction

The NDA group at NBL has finished developing and testing computer systems that calculate the isotopic abundances/enrichment of typical NBL Pu/U samples for verification purposes. Additional details of the software development and hardware systems can be found elsewhere^{1,2}. Results from the study suggest that the systems accurately assay the Pu/U isotopic abundances in a wide variety of samples, from 60% ²³⁹Pu to 95% ²³⁹Pu and from depleted U to 95% enriched U. In addition, the systems perform accurate assays with acquisition times from 15 minutes to 6 hours. This study reports the results of the NDA group tests.

Method of Analysis

The programs analyze the data by performing background subtraction, de-convolution of multiple peak structures, relative efficiency calculations, error analysis, and finally isotopic abundance measurements. The user has the option of specifying the type of background subtraction desired, fixing any of the parameters,

changing the regions of interest, and adding or deleting specific peaks to the region. At present, each program can analyze a region containing up to 1000 data points, and up to 12 γ or X-ray peaks.

The peak-fitting³ portion of the programs attempts to minimize the χ^2 between the fitting function and the data by utilizing a gradient search and the method of least-squares linearization of the fitting function with respect to the fitting parameters. The gradient search starts by calculating the χ^2 using program-determined values for the fitting parameters. Next, in an iterative manner, the program simultaneously increments all the fitting parameters by adjusting the relative magnitudes along the χ^2 gradient. After finding a relatively flat region of the χ^2 parameter space, the program employs the more sensitive method of linearization of the fitting function. Again, in an iterative manner, the program expands the fitting function in terms of the fitting parameters and uses the method of linear least squares to determine the optimum value for the parameters' increments. After each iteration in the analysis, the program calculates the local χ^2 value and compares the value with the previous χ^2 result. If the relative decrease of the χ^2 becomes less than some user defined amount, the fitting part of the program ends, storing the final peak-fitting parameters.

A Gaussian peak shape plus two exponential tailing functions describes each γ -ray peak shape, giving up to seven free parameters per peak¹. Mathematically one writes each peak as

$$Y_i = Y_0 e^{-\chi^2} + \delta (1 - e^{-\alpha' (x_i - x_0)^2}) \{ A e^{\beta (x_i - x_0)} + A' e^{\beta' (x_i - x_0)} \} \quad (1)$$

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 $\alpha(x_i - x_0)^2$,
- α is related to the gaussian standard deviation by $\alpha = 1/2\sigma^2$,
- α' is related to the gaussian standard deviation by $\alpha' = 1/5\sigma^2$,
- A and A' are the short and long term tailing amplitudes,
- β and β' are the short and long term tailing slopes,
- $\delta = 1$ for $x_i < x_0$, and 0 for $x_i > x_0$.

Since spectra may include X-rays, the programs must have the ability to fit X-ray peaks accurately as well. The peak shape for X-rays is somewhat more complicated. The convolution of a Gaussian with a Lorentzian

shaped peak describes each X-ray peak shape⁴. Because such a convolution has no closed form, the X-ray peak shape is approximated by

$$Y_i = Y_0 \{ [C_1 + C_2 \chi^2 + C_3 (1 - 2\chi^2)] e^{-\chi^2} + C_4 \beta(\chi) \} + tails \quad (2)$$

where C_1 , C_2 , C_3 , and C_4 are constants related to the α Gaussian parameter and the intrinsic width of the X-ray line (usually about 100 eV), and $\beta(\chi)$ is a function that approximates the non-integrable element of the convolution. In addition, like the γ -ray peaks, each X-ray peak has associated with it the same exponential tailing functions.

After the fitting part of the program finishes, the program uses the peak parameters to calculate the peak areas. The program integrates both the γ -ray and X-ray function forms, yielding a complete peak area. Mathematically, the γ -ray peak area is

$$AREA = Y_0 \sqrt{\frac{\pi}{\alpha}} + A \left(\frac{1}{\beta} - \frac{1}{2} \sqrt{\frac{\pi}{\alpha'}} \right) e^{\left(\frac{\beta}{2\sqrt{\alpha'}} \right)} \operatorname{erfc} \left(\frac{\beta^2}{4\alpha'} \right) \quad (3)$$

where erfc is the complementary error function. The X-ray peak area is

$$AREA = Y_0 \left[(C_1 + C_3) \sqrt{\frac{\pi}{\alpha}} + \frac{1}{2} (C_2 - 2C_3) \sqrt{\frac{\pi}{\alpha}} + C_4 B(\chi) \right] + Tails \quad (4)$$

where $B(\chi)$ is the integrated $\beta(\chi)$ function and $Tail$ is the integrated short tail functions as shown in equation 3.

General Description

In practice, the program infers at least three and up to five of the peak-fitting parameters from the detector-electronic system response. The programs permit the analyst to fix or free any combination of the peak parameters. For a Pu assay, PU-GAMMA utilizes the 59.536 keV ²⁴¹Am, the 129.293 keV ²³⁹Pu, and the 208.0 keV ²³⁷U-²⁴¹Am peaks to determine functional dependencies for α , A , β , A' , and β' . For a U assay, U-GAMMA utilizes the 185.72 keV ²³⁵U, the 147.52 keV ²³⁵U, and the stronger of the 63 or 59 keV peaks to determine

functional dependencies for α , A , β , A' , and β' . The programs contain the option to fit the background using a smoothed step-function approximation or a 3rd order polynomial.

A Pu sample spectrum contains 34 peaks with energies between 124 and 210 keV. Of these 34 peaks, 17 peaks are ^{239}Pu and eight of these 17 have sufficient intensity to use for the relative efficiency calculation. The program uses the eight ^{239}Pu γ -rays in order to calculate the relative efficiency of the detector-electronic system as a function of energy. The ratio of the peak area to the branching ratio of a specific ^{239}Pu peak defines the relative efficiency of the system as a function of energy, $R\epsilon(E)$. The program normalizes the relative efficiency to the 203.5 keV peak, calculates the efficiency of the other seven peaks relative to the 203.5 keV peak, and finally utilizes a 3rd order polynomial fit to relate the relative efficiency as a function of energy. Table I lists all the peaks of interest in the Pu spectrum, the region of interest the peaks appear in for fitting purposes, and whether or not the program uses the peak for the relative efficiency and isotopic calculations.

TABLE I				
Pu SPECTRUM γ -RAY PEAKS				
Region	Isotope	Energy (keV)	Rel. Eff.	Isotopic
1	^{239}Pu	124.510	No	No
1	^{239}Pu	125.210	No	No
1	^{241}Am	125.290	No	Yes
1,2	^{239}Pu	129.294	Yes	No
3	^{239}Pu	141.657	No	No
3	^{239}Pu	143.350	No	No
3	^{239}Pu	144.211	Yes	No
3	^{239}Pu	146.077	No	No
3	^{241}Am	146.557	No	No
3	^{241}Pu	148.567	No	Yes
3	^{241}Am	150.110	No	No
3,4	^{238}Pu	152.680	No	Yes
5	^{239}Pu	158.100	No	No

TABLE I (Continued)				
Pu SPECTRUM γ -RAY PEAKS				
Region	Isotope	Energy (keV)	Rel. Eff.	Isotopic
5	^{241}Pu	159.955	No	Yes
5	^{239}Pu	160.190	No	No
5	^{240}Pu	160.280	No	Yes
5	^{239}Pu	161.450	Yes	No
5	$^{241}\text{Am}, ^{237}\text{U}$	164.580	No	No
5	^{241}Am	165.930	No	No
6	^{241}Am	169.560	No	No
6	^{239}Pu	171.340	Yes	No
6	^{241}Am	173.100	No	No
6	^{241}Am	175.000	No	No
7	^{239}Pu	179.200	Yes	No
8	^{235}U	185.715	No	No
8	^{239}Pu	188.230	No	No
8	^{239}Pu	189.320	Yes	No
8	^{241}Am	191.900	No	No
9	^{239}Pu	193.130	No	No
9	^{239}Pu	195.660	Yes	No
9	^{241}Am	196.870	No	No
10	^{239}Pu	203.537	Yes	No
10	$^{241}\text{Am}, ^{237}\text{U}$	208.000	No	No

After calculating the relative efficiency and the remaining peak areas, the program uses the 152.7-keV, 159.96-keV, 160.3-keV, and 148.6-keV γ -ray peak areas to calculate the relative abundance of ^{238}Pu , ^{240}Pu , and ^{241}Pu to ^{239}Pu . One can only calculate the relative abundance of ^{242}Pu using ^{239}Pu , ^{240}Pu , and ^{241}Pu isotopic abundances; since ^{242}Pu is a very weak γ -ray emitter. Correlations between the various abundances and the ^{242}Pu exist and one exploits these correlations to estimate the ^{242}Pu abundance. Recent work at NBL suggests that the 242 abundance can be fit using a correlation of

$$242 = \frac{K_1 (240) (241)}{(239)} + \frac{K_2 (240) (241)}{(239)^2} \quad (5)$$

For a U sample spectrum, the analysis concentrates on the region between 20 and 85 keV. In this region there are 15 γ and X-ray peaks of interest, including five ^{231}Th peaks. Table II lists all the peaks of interest in the U spectrum.

TABLE II				
U SPECTRUM γ AND X-RAY PEAKS				
Region	Isotope	Energy (keV)	Rel. Eff.	Isotopic
1	^{231}Pa	24.210	No	No
1	^{231}Th	25.640	Yes	No
1	^{231}Pa	27.300	No	No
2	^{236}U	49.370	No	Yes
2	^{238}U	49.550	No	Yes
3	^{234}U	53.200	No	Yes
4	^{231}Th	58.570	Yes	No
4	^{236}U	59.100	No	Yes
5	^{234}Th	63.280	No	Yes
6	^{230}Th	67.672	No	No
7	^{231}Th	81.220	Yes	No
7	^{231}Th	82.080	Yes	No
7	X-ray	83.210	No	No
7	^{231}Th	84.200	Yes	No
7	Pb K_β	84.900	No	No

Analogous with the Pu analysis, the program uses the five ^{231}Th peaks to calculate the detector's relative efficiency over the energy range. Then, using the ^{234}U γ -ray at 53.3 keV, the ^{236}U γ -rays at 49.4 and 59.10 keV, the ^{238}U γ -ray at 49.6 keV and the ^{234}Th (in equilibrium with ^{238}U) γ -ray 63.3 keV peak areas; the program calculates the relative abundance of ^{234}U , ^{236}U , and ^{238}U . In addition, U-GAMMA utilizes previous work performed at NBL^{5,6} to calculate the ^{235}U enrichment. In the first case, the program uses a functional

relation of the 90 keV to 92 keV peak to calculate the enrichment. In the second case, the program uses a functional relation of the 63.3 keV to 586 keV peak.

Results

For Pu results, NBL tested the program by analyzing 12 spectra of four IRMM standards measured with three different detector systems. Table III shows the results. The top entry in each cell is the value obtained using PU-GAMMA, the lower entry is the standard certified value decayed to the appropriate date. The last column shows the calculated specific power of the sample, again compared with the standard certified value. In all cases the agreement between the standard isotopic abundances and the measured isotopic abundances is good. Finally, the significant value to compare between measured result and standard value is the specific power. Agreement between these values is excellent. For the 93% and 84% ²³⁹Pu standard, the measured errors were approximately 3%, for the 74% and 61% ²³⁹Pu standard, the measured errors were approximately 4%.

TABLE III						
PU ISOTOPIC ABUNDANCE/SPECIFIC POWER RESULTS						
Detector	%238	%239	%240	%241	%242	Power (W/g)
APTC std.	.011	93.32	6.47	0.160	0.037	.0025
	.011	93.49	6.29	0.162	0.039	.0025
LEPS std.	.012	93.16	6.62	0.170	0.040	.0025
	.011	93.50	6.29	0.161	0.039	.0025
REGE std.	.010	93.40	6.40	0.155	0.035	.0024
	.011	93.50	6.29	0.161	0.039	.0025
APTC std.	0.064	84.66	14.17	0.737	0.361	.0036
	0.067	84.64	14.19	0.745	0.354	.0036
LEPS std.	0.063	84.33	14.45	0.768	0.383	.0036
	0.067	84.64	14.19	0.745	0.354	.0036
REGE std.	0.065	84.38	14.44	0.744	0.371	.0035
	0.067	84.64	14.19	0.743	0.354	.0036

TABLE III (Continued)						
PU ISOTOPIC ABUNDANCE/SPECIFIC POWER RESULTS						
Detector	%238	%239	%240	%241	%242	Power (W/g)
APTC std.	0.770 0.821	74.31 74.56	18.59 18.52	3.92 4.01	2.40 2.09	.0103 .0106
LEPS std.	0.695 0.821	75.49 74.57	18.05 18.52	3.61 4.00	2.16 2.09	.0102 .0106
REGE std.	0.821 0.821	72.73 74.57	19.54 18.52	4.23 4.00	2.68 2.09	.0103 .0106
APTC std.	1.07 1.17	65.94 63.86	24.87 25.82	4.77 4.93	3.35 4.23	.0134 .0136
LEPS std.	1.09 1.17	64.93 63.87	25.61 25.83	4.92 4.91	3.45 4.23	.0135 .0136
REGE std.	1.28 1.17	62.43 63.87	26.81 25.82	5.66 4.91	3.81 4.23	.0138 .0136

For U results, NBL tested the program by calculating the enrichment of eight known U foil samples. Additionally, the NDA group tested the effect of placing the foil samples in a steel can, mimicking sealed samples. Finally, the group tested the effect of various data acquisition times on the enrichment calculation. Tables IV and V show the results of the enrichment analysis. Agreement between the known sample enrichments and calculated enrichments is excellent for most cases.

TABLE IV				
COMPARISON BETWEEN NBL AND U STANDARDS				
Trial	Time (min)	Std. Foil	NBL	error
REGE				
1	60	5.000%	4.914%	0.127%
2	60	10.000%	9.980%	0.277%
3	60	21.000%	21.042%	0.557%

TABLE IV (Continued)				
COMPARISON BETWEEN NPL AND U STANDARDS				
Trial	Time (min)	Std. Foil	NBL	error
4	60	40.000%	40.860%	1.153%
5	60	60.000%	61.608%	0.490%
6	60	80.000%	80.748%	0.727%
7	60	91.000%	90.773%	0.651%
8	60	93.000%	91.757%	0.891%
APTC				
1	60	5.000%	4.579%	0.306%
2	60	10.000%	9.549%	0.869%
3	60	21.000%	21.334%	1.197%
4	60	40.000%	42.149%	1.285%
5	60	60.000%	62.234%	1.391%
6	60	80.000%	82.013%	1.216%
7	60	91.000%	91.171%	1.399%
8	60	93.000%	96.943%	1.014%
LEPS				
1	60	5.000%	4.050%	0.415%
2	60	10.000%	10.816%	0.864%
3	60	21.000%	22.663%	6.002%
4	60	40.000%	42.519%	1.730%
5	60	60.000%	62.130%	1.169%
6	60	80.000%	82.240%	2.246%
7	60	91.000%	89.038%	1.137%
8	60	93.000%	91.215%	0.966%
REGE				
1	30	5.000%	4.632%	0.158%

TABLE IV (Continued)				
COMPARISON BETWEEN NBL AND U STANDARDS				
Trial	Time (min)	Std. Foil	NBL	error
2	30	10.000%	10.642%	1.714%
3	30	21.000%	22.897%	0.987%
4	30	40.000%	44.220%	1.503%
5	30	60.000%	64.174%	1.226%
6	30	80.000%	81.205%	0.772%
7	30	91.000%	89.973%	1.337%
8	30	93.000%	91.222%	1.014%
APTC				
1	30	5.000%	5.098%	1.804%
2	30	10.000%	9.271%	1.505%
3	30	21.000%	19.995%	2.388%
4	30	40.000%	44.089%	4.727%
5	30	60.000%	63.329%	6.777%
6	30	80.000%	85.607%	3.090%
7	30	91.000%	90.345%	1.798%
8	30	93.000%	96.184%	1.765%
LEPS				
1	30	5.000%	3.580%	0.522%
2	30	10.000%	10.577%	0.422%
3	30	21.000%	21.325%	1.239%
4	30	40.000%	44.132%	0.750%
5	30	60.000%	62.776%	1.206%
6	30	80.000%	80.195%	0.808%
7	30	91.000%	92.059%	1.153%
8	30	93.000%	93.161%	0.957%

TABLE IV (Continued)				
COMPARISON BETWEEN NBL AND U STANDARDS				
Trial	Time (min)	Std. Foil	NBL	error
REGE				
1	15	5.000%	4.932%	0.234%
2	15	10.000%	11.138%	2.021%
3	15	21.000%	23.764%	1.107%
4	15	40.000%	45.173%	2.250%
5	15	60.000%	64.401%	3.276%
6	15	80.000%	79.229%	1.099%
7	15	91.000%	92.088%	0.971%
8	15	93.000%	89.307%	2.290%
APTC				
1	15	5.000%	4.785%	0.509%
2	15	10.000%	10.617%	0.660%
3	15	21.000%	22.769%	1.578%
4	15	40.000%	40.025%	2.140%
5	15	60.000%	63.598%	2.078%
6	15	80.000%	82.101%	5.883%
7	15	91.000%	89.526%	2.507%
8	15	93.000%	87.679%	1.807%
LEPS				
1	15	5.000%	4.864%	0.759%
2	15	10.000%	8.883%	0.519%
3	15	21.000%	21.279%	1.424%
4	15	40.000%	42.393%	1.265%
5	15	60.000%	62.309%	1.479%
6	15	80.000%	82.974%	1.269%

TABLE IV (Continued)				
COMPARISON BETWEEN NBL AND U STANDARDS				
Trial	Time (min)	Std. Foil	NBL	error
7	15	91.000%	92.965%	1.486%
8	15	93.000%	92.667%	1.804%
REGE				
1	5	5.000%	5.545%	0.952%
2	5	10.000%	10.474%	0.714%
3	5	21.000%	22.659%	2.402%
4	5	40.000%	45.525%	1.664%
5	5	60.000%	62.819%	1.970%
6	5	80.000%	81.148%	3.949%
7	5	91.000%	83.486%	2.213%
8	5	93.000%	94.124%	2.010%
APTC				
1	5	5.000%	7.009%	1.655%
2	5	10.000%	10.936%	2.438%
3	5	21.000%	26.882%	11.512%
4	5	40.000%	52.020%	4.192%
5	5	60.000%	67.254%	7.853%
6	5	80.000%	86.021%	8.376%
7	5	91.000%	99.918%	9.398%
8	5	93.000%	77.400%	6.328%
LEPS				
1	5	5.000%	----	----
2	5	10.000%	12.088%	1.194%
3	5	21.000%	24.715%	2.389%
4	5	40.000%	44.091%	1.708%

TABLE IV (Continued)				
COMPARISON BETWEEN NBL AND U STANDARDS				
Trial	Time (min)	Std. Foil	NBL	error
5	5	60.000%	57.325%	3.235%
6	5	80.000%	78.351%	2.358%
7	5	91.000%	98.297%	5.198%
8	5	93.000%	95.459%	1.645%

TABLE V				
COMPARISON OF U FOIL STANDARDS IN CANS WITH RESULTS				
Trial	Time (min)	Std. Foil	NBL	error
REGE				
1	60	5.000%	4.744%	7.487%
2	60	10.000%	10.918%	11.436%
3	60	21.000%	23.305%	3.910%
4	60	40.000%	43.953%	5.082%
5	60	60.000%	61.412%	1.135%
6	60	80.000%	81.628%	0.898%
7	60	91.000%	89.727%	0.735%
8	60	93.000%	93.183%	0.623%
APTC				
1	60	5.000%	5.130%	1.169%
2	60	10.000%	9.409%	0.323%
3	60	21.000%	22.127%	1.469%
4	60	40.000%	39.805%	1.455%

TABLE V (Continued)				
COMPARISON OF U FOIL STANDARDS IN CANS WITH RESULTS				
Trial	Time (min)	Std. Foil	NBL	error
5	60	60.000%	60.399%	1.175%
6	60	80.000%	81.816%	2.240%
7	60	91.000%	93.512%	1.117%
8	60	93.000%	93.304%	0.553%
LEPS				
1	60	5.000%	5.768%	5.033%
2	60	10.000%	9.609%	0.352%
3	60	21.000%	20.411%	0.994%
4	60	40.000%	39.848%	0.552%
5	60	60.000%	62.629%	1.320%
6	60	80.000%	83.176%	0.653%
7	60	91.000%	92.573%	1.208%
8	60	93.000%	94.517%	0.927%
REGE				
1	30	5.000%	3.628%	7.449%
2	30	10.000%	10.886%	16.511%
3	30	21.000%	23.160%	1.548%
4	30	40.000%	44.253%	2.022%
5	30	60.000%	64.031%	0.719%
6	30	80.000%	81.237%	1.578%
7	30	91.000%	91.469%	1.180%
8	30	93.000%	93.406%	11.540%
APTC				
1	30	5.000%	----	----
2	30	10.000%	----	----

TABLE V (Continued)				
COMPARISON OF U FOIL STANDARDS IN CANS WITH RESULTS				
Trial	Time (min)	Std. Foil	NBL	error
3	30	21.000%	21.710%	0.941%
4	30	40.000%	40.334%	1.277%
5	30	60.000%	59.963%	2.126%
6	30	80.000%	79.576%	1.459%
7	30	91.000%	91.687%	2.167%
8	30	93.000%	91.318%	1.412%
LEPS				
1	30	5.000%	4.767%	0.266%
2	30	10.000%	9.372%	0.368%
3	30	21.000%	19.186%	0.999%
4	30	40.000%	42.479%	0.964%
5	30	60.000%	60.097%	1.007%
6	30	80.000%	79.635%	0.860%
7	30	91.000%	90.582%	1.141%
8	30	93.000%	92.941%	0.907%
REGE				
1	15	5.000%	2.334%	1.393%
2	15	10.000%	11.421%	1.573%
3	15	21.000%	19.344%	2.629%
4	15	40.000%	42.564%	1.131%
5	15	60.000%	65.069%	2.893%
6	15	80.000%	83.290%	0.825%
7	15	91.000%	90.241%	1.169%
8	15	93.000%	92.823%	6.738%
APTC				
1	15	5.000%	5.674%	0.849%

TABLE V (Continued)				
COMPARISON OF U FOIL STANDARDS IN CANS WITH RESULTS				
Trial	Time (min)	Std. Foil	NBL	error
2	15	10.000%	9.455%	0.986%
3	15	21.000%	17.983%	1.517%
4	15	40.000%	41.997%	1.694%
5	15	60.000%	63.600%	2.228%
6	15	80.000%	82.792%	1.859%
7	15	91.000%	80.220%	3.031%
8	15	93.000%	84.472%	2.329%
LEPS				
1	15	5.000%	4.344%	0.403%
2	15	10.000%	10.078%	0.768%
3	15	21.000%	17.271%	1.361%
4	15	40.000%	42.798%	1.655%
5	15	60.000%	62.821%	1.961%
6	15	80.000%	81.261%	1.193%
7	15	91.000%	87.028%	1.904%
8	15	93.000%	95.870%	1.855%

Summary

PU-GAMMA and U-GAMMA are computer programs utilizing advanced peak-fitting techniques and additional operator interaction to provide accurate, rapid Pu and U isotopic abundance calculations. The NDA group designed the program to give detailed fits for complex multiple peak regions, ultimately yielding isotopic/enrichment information. The analysis of Pu and U data shows that the programs achieve a high level of accuracy.

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UPGRADE OF THE NEW BRUNSWICK LABORATORY CONTROLLED-POTENTIAL COULOMETRIC METHOD FOR PLUTONIUM

P. V. Croatto and H. D. Troutman

NBL utilizes a controlled-potential coulometric technique for the accurate and precise determination of plutonium.^{1,2} The controlled-potential coulometer has been upgraded in recent years to improve the system performance. The identification of systematic errors in the analog integrator³ used in the first generation NBL coulometer led to the development of the FH1 digital integrator.^{4,5} The digital integrator was incorporated with commercially available potentiostats and other components to constitute the second generation NBL coulometer, a computer-assisted coulometric system.⁶ The automated coulometer system was updated with modern, high-quality electronic components to produce the third generation NBL coulometer which has been evaluated relative to the second generation system in terms of reproducibility of results for plutonium analysis.⁷

Recently, one of the three third generation NBL coulometer systems has been further upgraded, thoroughly tested, and is in operation. The HP9000-Model 226 computer has been replaced with a HP PC-313CM BASIC Controller on a HP Vectra 386s/20 computer. An IOTech Digital I/O interface was also needed for the upgrade. Other changes included a printer upgrade and software enhancements. HP BASIC 6.2 replaced HP BASIC 3.0 and this required modifications to the instrument control program. Further software enhancement was added by HP BASIC PLUS which provides visual objects that aid in the collection, analysis, and presentation of data. Work on this project will continue next year to upgrade the other two coulometry systems.

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PREPARATION OF SAMPLES FOR MASS SPECTROMETRY

I. Frank, V. E. Connolly, M. M. Smith, and A. V. Stiffin

The isotopic content of uranium in samples received at NBL is determined by thermal ionization mass spectrometry (TIMS). The uranium in the samples is prepared for TIMS analysis by purification using an ether-extraction process.¹ This procedure, although it produces good results, may not remove elemental or molecular impurities found in some samples. The impurities could affect the MS burn characteristics and produce isobaric interferences, altering the isotopic ratios used in computing the composition of the uranium. In addition, the amount of uranium recovered is not known precisely, leading to imprecision in loading the sample on the spectrometer filament. NBL is evaluating an ion-exchange method using U/TEVA-Spec™ resin which promises both more complete recovery of the uranium from the sample, and a purer uranium TIMS preparation, thereby increasing the accuracy of the isotopic measurements.

In a previous short study, it was shown that the U/TEVA-Spec™ resin removes impurities, producing a pure uranium preparation and excellent TIMS analyses.² In the past year, a statistically-controlled study has begun. In the first phase of the study, the effect of acid concentration on sample recovery was evaluated using known amounts of three pure uranium materials. Solutions with nitric acid concentrations of 1.5M, 2.0M, and 2.5M were used to load samples to the resin column and to rinse the column to remove impurities. Uranium was eluted from the columns with 0.01M nitric acid. The eluted material was then dried and analyzed for uranium using the NBL Titrimetric Method³. In each case, uranium recovery was greater than 98%.

In the second phase of the study, three samples containing significant amounts of impurities were dissolved in 2.5M nitric acid, purified using the resin, and again measured for uranium content by the NBL Titrimetric Method. The NBL Titrimetric Method had been used previously to assay the unpurified samples. In each case uranium recovery was greater than 96%. In addition, one sample, which had been difficult to titrate before ion-exchange, was easily analyzed after purification.

In the final phase of this project, a statistical study was designed using a set of three samples containing significant impurities, and an TIMS standard uranium preparation. The purpose of this study was to qualify the U/TEVA-Spec™ method by comparing the results obtained on these samples to results obtained on the same samples using the ether-extraction method. Several portions of each sample were purified by the ether-extraction method and several by the U/TEVA-Spec™ method. These purified materials will be analyzed by TIMS, and the results then compared. If there is no statistically significant difference between TIMS results obtained by the two methods, the U/TEVA-Spec™ method will be considered qualified to use in performing reportable measurements.

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ELIMINATION OF DICHROMATE FROM URANIUM TITRIMETRIC MEASUREMENTS

J. P. Zebrowski, L. D. Preston, K. D. Johnson, G. J. Orłowicz,
K. S. Scheldelman, and M. M. Smith

The NBL-Modified Davies and Gray Titrimetric Method¹ (commonly called the NBL Titrimetric Method) is a standard method of uranium analysis. In this procedure, uranium is reduced to U(IV) and is titrated with potassium dichromate to U(VI). Hexavalent chromium compounds are considered human carcinogens; when mixed with radioactive materials they form RCRA mixed waste. In the NBL Titrimetric Method, the hexavalent chromium titrant is reduced by uranium; thus titrated uranium samples do not contain hexavalent chromium. Nevertheless, with the current regulatory environment, it is extremely difficult for NBL to dispose of these waste materials.

To eliminate this disposal problem, NBL has been evaluating alternative titrimetric procedures that would not use potassium dichromate. Two different approaches, both of which used Ce(IV) stabilized in sulfuric acid as the titrant, were identified. The first method evaluated was based on a method used at Rocky Flats². The second method evaluated was based on a method developed at Los Alamos National Laboratory³ (LANL) and involved the direct substitution by the Ce(IV) titrant for the dichromate titrant in the NBL Titrimetric Method.

The Ce(IV) titrants, for this work, were prepared from $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, since this reagent can be obtained in high purity. The Ce(IV) in the titrant was stabilized in a 1M sulfuric acid medium^{4,5}. The prepared solutions were allowed to stand for two weeks to allow a minor insoluble solid to settle out. The titrant solutions were then drawn off and filtered into a second bottle. Preliminary titrations involved obtaining a calibration factor for the titrants (mg U/g titrant) using uranium standards via the two procedures and then calculating the precision.

Results from preliminary titrations indicated that there were unidentified problems with NBL's attempt to use the Rocky Flats procedure that resulted in poor precision. Additionally, it became apparent that the method was not well suited for dealing with oxidizable sample impurities. Since NBL must analyze all types of sample materials, this would limit the possible applications of the procedure in our Laboratory. On the other hand, the NBL Titrimetric Method is known to be capable of handling many interferences. Directly substituting the Ce(IV) titrant for the dichromate in the NBL Titrimetric Method also gave satisfactory results in the preliminary titrations. Titration curves were experimentally derived and indicated there was no difference between the potentiometrically determined endpoints of the Ce(IV) and the potassium dichromate titrations. Ten titrations of known samples (prepared from certified uranium metal) using a 0.03M Ce(IV) titrant resulted in a titrant calibration factor with an overall relative standard deviation of 0.023% which compared favorably to the precision normally obtained using standardized potassium dichromate. Based on these results, the NBL Titrimetric Method using Ce(IV) as the titrant was chosen for further study.

Draft procedures for both the preparation of the Ce(IV) titrant and for the titrimetric method have been written and a statistical plan, that allows a direct comparison of the dichromate and the cerium titration procedures, has been developed. The accuracy and precision of the method will be examined by assay of primary standard uranium metal. Upon successful validation of the method, the effects of chemical interferences on the method's performance will be evaluated. Additionally, the long term stability of the titrant will be investigated.

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INSTALLATION AND TESTING OF A KINETIC PHOSPHORESCENCE ANALYZER

P. V. Croatto and I. W. Frank

A Chemchek Kinetic Phosphorescence Analyzer (KPA) has been purchased, set-up, and tested for the determination of ng/L to mg/L levels of uranium in aqueous solutions. This KPA instrument will replace the fluorescence Scintrex UA-3 Uranium Analyzer currently used at the laboratory. Routine analyses can be easily and effectively accomplished using the KPA, with accuracy and precision greater than the NBL fluorometric determination¹ using the Scintrex UA-3 and without the need for internal standards. Samples can be analyzed directly or with limited sample preparation. Chemical separations are only required for very low levels of uranium in samples with complex matrix.

The KPA instrument has been modified by replacing the europium emission filter with a uranium emission filter. This allows the preparation and use of "in-house" uranium reference standards which are traceable. In addition to providing direct traceability, there are two additional advantages to this modification: it eliminates the need to periodically purchase europium standards, and it also avoids the stability problems associated with this standard.

The instrument has been calibrated to cover the concentration range of $4.0 \times 10^{-4} \mu\text{g}$ to $4.0 \mu\text{g}$ U/g of solution. Preliminary results, using knowns and blinds, were well within $\pm 5\%$ RSD. The KPA method is much easier than the fluorometry method since no heating or heating times have to be established and standard addition is not needed for most samples. The next task involves the statistical evaluation of the KPA method. Future plans include measuring lanthanides and adapting the instrument for glovebox operation.

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INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER INSTALLATION AND ACCEPTANCE TESTING

F. E. Jones, J. W. Gramlich, and A. M. Voeks

A VG/Fisons PlasmaQuad PQ2+, Inductively Coupled Plasma Mass Spectrometer (ICP-MS), has been installed and tested in the Plutonium section of New Brunswick Laboratory (NBL). This instrument will be used for the measurement of impurity levels in transuranic-containing materials at NBL. This instrument has great potential for analyzing samples related to the DOE environmental restoration program. The NBL instrument is in a glovebox specially designed to contain the transuranic (or other radioactive or toxic) materials. The glovebox is modeled after the design used at LANL, however, additional modifications have been incorporated to improve sample handling and maintenance of the plasma torch. A manufacturer of ICP-MS instruments has expressed an interest in the design of the glovebox for use by prospective customers desiring to make ICP-MS measurements on radioactive samples.

The instrument has demonstrated sub-parts per billion sensitivity and has passed all acceptance tests. Additional testing and modifications (to insure safety) will be conducted before the instrument will be used to analyze radioactive materials.

INSTALLATION AND TESTING OF A URANIUM HEXAFLUORIDE MASS SPECTROMETER

F. E. Jones, P. V. Croatto, and J. W. Gramlich

New Brunswick Laboratory has obtained a state-of-the-art Finnigan MAT281 uranium hexafluoride mass spectrometer (UF_6 MS) from Westinghouse Materials in Fernald, Ohio. The installation of UF_6 MS instrument has been completed. The UF_6 MS was powered-up and functioned as anticipated.

Approval was obtained for an operational safety procedure that covered the initial performance testing of the instrument. Measurements and tests have begun to certify that the UF_6 MS can meet operational specifications necessary to perform state-of-the-art precision uranium isotopic abundance measurements.

A total of eleven tests will be used in this certification. Five tests have already been completed and the results meet or exceed the specifications. Operational specification testing will continue during FY 94.

NBL has also obtained fifty-seven cylinders containing thirty enrichment levels of the Portsmouth "UF₆ working-standards" from Westinghouse Materials in Fernald, Ohio. These standards contain ²³⁵U enrichments from 2.3 to 10.4 weight percent. These cylinders contain 20 to 100 grams of UF₆ and can be connected directly to the UF₆ MS and used for calibration and analyses.

DEVELOPMENT OF A RADIOACTIVE DECAY CHAIN SPREADSHEET WITH THE INCLUSION OF ALL DAUGHTER AND STABLE ISOTOPES

D. Eckelkamp-Baker and D. T. Baran

Introduction

In order to calculate an approximate activity of material being shipped, the NDA group at NBL developed a spreadsheet utilizing the Bateman equations¹. This spreadsheet calculated the amount of material for the parent and each subsequent daughter in the specific Th, U, Pu, and Am decay chains. However, this initial spreadsheet employed only single branch decays, assuming each isotope decayed only through α or β decay. In most cases, such a solution gives accurate enough results for shipping purposes (total sample activity), but it is not the complete solution. The complete solution includes dual branch decays determined by calculating material generated and subsequently decayed through both the α and β paths.

The NDA group recently completed the development of a spreadsheet DECAYALL which details the complete radioactive decay (parent, all daughters, and stable progeny) of any Th/U/Pu/Am input sample. Input includes the mass amount of material present and the isotopic abundances of the material present at time t_0 , and the length of decay time Δt . The output includes the mass, atom number, and activity of all subsequent decays, from parent through stable daughter.

Theory

The basic empirical equation governing radioactive decay is

$$\frac{dN(t)}{dt} = -\lambda N \quad (6)$$

Here, N is the number of atoms and λ is the decay constant. If N_1^0 is the number of atoms present at time $t = 0$ then the solution becomes

$$N(t) = N^0 e^{-\lambda t} \quad (7)$$

If the daughter remains stable then the number of atoms, as a function of time, is

$$N_2(t) = N_1^0 (1 - e^{-\lambda_1 t}) \quad (8)$$

where the subscripts 1 and 2 refer to the parent and daughter, respectively.

If the daughter isotope also decays the governing equation becomes

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad (9)$$

Solving this equation, again assuming no daughter present at time $t = 0$, leads to

$$N_2(t) = N_1^0 \frac{\lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (10)$$

As the decay chain grows longer, the mathematics becomes tedious. However, one can identify a pattern summarized by the Bateman equations. If one writes the general differential equation for each parent-daughter pair as

$$\frac{dN_k}{dt} = \lambda_{k-1} N_{k-1} - \lambda_k N_k \quad (k > 1) \quad (11)$$

then the general solution, again assuming no daughters present at time $t = 0$, becomes

$$N_k(t) = N_1^0 \prod_{i=1}^{k-1} \lambda_i \sum_{i=1}^k C_i e^{-\lambda_i t} \quad (k > 1) \quad (12)$$

where $N_k(t)$ is the number of atoms of the k th isotope after time t , and

$$C_i = \prod_{j=1}^k \frac{1}{\lambda_j - \lambda_i} \quad (j \neq i) \quad (13)$$

For $k = 1$, the first isotope in the chain the solution is always

$$N_1(t) = N_1^0 e^{-\lambda_1 t} \quad (14)$$

Finally, the series terminates with the last, stable isotope, mathematically represented by the solution to

$$\frac{dN_k}{dt} = \lambda_{k-1} N_{k-1} \quad (15)$$

The presence of one or more daughter isotopes at $t = 0$ requires a chain decay solution for each daughter with the daughter as the first isotope in the chain. The total solution becomes the sum of the appropriate chain solutions. Consequently, the most general solution for chain decays, without branching, for the k th isotope is

$$\begin{aligned} N_k(t) &= N_k^0 + \sum_{m=1}^{k-1} \left[N_m^0 \prod_{i=m}^{k-1} \lambda_i \sum_{j=m}^k C'_j e^{-\lambda_i t} \right] \\ &= N_k^0 + \sum_{m=1}^{k-1} \left[N_m^0 \prod_{i=m}^{k-1} \lambda_i \sum_{j=m}^k \left[\left(\prod_{j=m, j \neq i}^k \frac{1}{\lambda_j - \lambda_i} \right) e^{-\lambda_i t} \right] \right] \end{aligned} \quad (16)$$

where the product indices for C_i are slightly changed so that C'_i is defined as

$$C'_i = \prod_{j=m, j \neq i}^k \frac{1}{\lambda_j - \lambda_i} \quad (17)$$

Branching Ratios

A branching decay occurs when an isotope decays with measurable probability by both α or β emission. In this case, the decay constant λ for the parent breaks down to $\lambda = \lambda_\alpha + \lambda_\beta$. The partial constants are additive because the decay modes are independent. Therefore, one defines the branching ratios as $BR_\alpha = \lambda_\alpha/\lambda$ and $BR_\beta = \lambda_\beta/\lambda$.

The basic decay equation becomes

$$\begin{aligned}\frac{dN(t)}{dt} &= -\lambda_{\alpha}N - \lambda_{\beta}N \\ &= -(\lambda_{\alpha} + \lambda_{\beta})N\end{aligned}\quad (18)$$

with the solution having the form

$$\begin{aligned}N(t) &= N^0 e^{-\lambda_{\alpha}t} e^{-\lambda_{\beta}t} \\ &= N^0 e^{-(\lambda_{\alpha} + \lambda_{\beta})t}\end{aligned}\quad (19)$$

assuming the daughters are stable. Figure 1 schematically represents such a decay.

Figure 1

In Figure 1, 1 represents the parent and 2α and 2β represent the daughter isotopes produced by α and β emission, respectively. From equation (13) one finds the solution for isotope 1

$$N_1(t) = N_1^0 e^{-\lambda_1 t} \quad (20)$$

which agrees with equation (9). The equation governing the production of the α (or β) produced isotope is

$$\frac{dN_{2\alpha}}{dt} = +\lambda_{1\alpha}N_1 \quad (21)$$

where $\lambda_{1\alpha} = \lambda_1 BR_{\alpha}$, and one knows $N_1(t)$ from equation (15). Substituting gives

$$\frac{dN_{2\alpha}}{dt} = BR_{\alpha} N_1^0 \lambda_1 e^{-\lambda_1 t} \quad (22)$$

and solving yields

$$\int_{initial}^{final} dN_{2\alpha} = BR_{\alpha} N_1^0 \lambda_1 \int_0^t e^{-\lambda_1 t} dt$$

$$N_{2\alpha}(t) - N_{2\alpha}(0) = BR_{\alpha} N_1^0 \lambda_1 \left(\frac{-1}{\lambda_1} \right) e^{-\lambda_1 t} \Big|_0^t \quad (23)$$

Assuming no daughter isotope present at time $t = 0$, then $N_{2\alpha}(0) = 0$ and equation (18) simplifies to

$$N_{2\alpha} = BR_{\alpha} N_1^0 (1 - e^{-\lambda_1 t}) \quad (24)$$

and equivalently for the β produced isotope

$$N_{2\beta} = BR_{\beta} N_1^0 (1 - e^{-\lambda_1 t}) \quad (25)$$

The form of equations (19) and (20) shows similarity to the solution for a decay with no branching and the addition of the branching ratio factor. One rewrites Equations (19) and (20) as

$$N_{2\alpha} = N_{1\alpha}^0 (1 - e^{-\lambda_1 t})$$

$$N_{2\beta} = N_{1\beta}^0 (1 - e^{-\lambda_1 t}) \quad (26)$$

where $N_{1\alpha}^0 = BR_{\alpha} N_1^0$ and $N_{1\beta}^0 = BR_{\beta} N_1^0$. In this case, the branching ratio scales the number of initial atoms present and not the decay constants. Consequently, the calculations use the full decay constant (λ) in both chains. In general, isotopes 2α and 2β also decay. However, each decay in such a manner that the daughter from the decay is the same isotope. The branch closes back to a single isotope. Typically, isotope 2α β decays and isotope 2β α decays to the same daughter, giving two parallel paths from isotope 1 to isotope 3. For example, ^{227}Ac α decays to ^{223}Fr which in turn β decays to ^{223}Ra . ^{227}Ac also β decays to ^{227}Th which, in turn, α decays to ^{223}Ra . Since the two paths are parallel and independent, the number of 3's produced equal the sum of 3α and 3β .

Schematically then, one uses the equivalent system to solve the real decay shown in Figure 2.

Figure 2

Therefore, given some decay chain, which includes some branching decays; one can construct an equivalent system (or systems) using the appropriate branching ratios. From this example, it is easy to see that the similarity continues for longer decay chains.

With the exception of equations (11) and (12), one assumes that at $t = 0$ only the parent isotope is present in the decay chain. Such an assumption is both unrealistic and incomplete. Accounting for the presence of other isotopes at $t = 0$ is not difficult, requiring setting up a separate decay chain and its equivalent systems for each isotope as the first of the chain. As indicated previously, the complete solution is a sum of all the branches and chains.

Decayall

The specific decay chains of interest are ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{242}Pu , and ^{241}Am . The spreadsheet requires three types of user inputs, the Initial Mass (in grams) of each isotope in the sample to be decayed, the Decay Time, and the Isotopic Composition as a percentage of the specific element. The spreadsheet allows any combination of amounts and isotopes and then calculates the Initial # of Atoms for each isotope. The spreadsheet also allows input of any combination of years, days, hours, minutes, seconds and milliseconds for the Decay Time. The spreadsheet calculates and shows Total (sec), which is the total time in seconds, by using the appropriate factors listed under Conversions. The spreadsheet uses Conversions, Avogadro's Number and each isotope's Atomic Mass, Half Life and Branching Ratio as numerical constants in the calculations. The spreadsheet calculates the Specific Activities for each isotope using its half life and shows the Total Mass (in grams) for the whole sample.

The spreadsheet first calculates the Final # of Atoms values from the given input values and the equivalent systems' decays and then calculates each isotope's Final Mass (g) and Activities. The spreadsheet also shows error checking which is a summary of various internal error-checking done to the equivalent systems calculations. In addition, the spreadsheet performs a check to ensure that the total Initial # of Atoms and total Final # of Atoms agree within calculational limits. In addition, the spreadsheet generates four printed reports. The **Input Values Summary** and the **Output Values Summary** are single page reports. The **Input Values Detail** and **Output Values Detail** reports contain all of the given and calculated isotopic and elemental information. The error checking done here ensures that values carried over from one page to another remain consistent.

Figure 3 shows an example of the **Input Values Summary** report and figure 4 shows an example of the **Output Values Summary** report. The **Input Values Detail** report example is figure 5 and the **Output Values Detail** example is in figure 6.

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UNKNOWN OR BLIND URANIUM STANDARDS FOR USE WITH THE NBL HIGH-PRECISION TITRIMETRIC METHOD

W. Nichiporuk, K. S. Scheidelman, P. V. Croatto, and M. M. Smith

The NBL Quality Assurance Program requires that, where feasible, unknown or blind standards be used as the quality control standards upon which accept/reject decisions are based for reportable measurements.¹ Known standards, prepared by the user, are normally used for checking the adequacy of the equipment and reagents or for preliminary testing and evaluation of a method, instrument, or measurement system. For the NBL High-Precision Titrimetric Method,² known standards have also been used as quality control standards because a program for blind standards had not been developed. A blind standards program for this method has now been developed to better meet the requirements of the NBL Quality Assurance Manual. The project to develop this program consisted of the design, preparation, and blinding to the analysts of traceable uranium standards. The blinded standards were then used in a statistical study to establish quality control limits for the NBL High-Precision Titration Method.

In accordance with the statistical design, three analysts participated in the study. One analyst prepared the all the samples. Uranium metal pieces of CRM 112-A between 2.5 and 3.5 grams weight were cleaned, weighed and dissolved in beakers per High-Precision Titrimetric Procedure specifications.² A total of 26 samples were prepared and divided between two analysts for sample assay following the NBL High-Precision Procedure. The statistical plan involved titrating these blinds and six knowns over two days using a prescribed scheme for each day.³

Knowns

The results of all knowns were within the established laboratory limits for high precision titration of $\pm 0.009\%$. The results of the individual analyses are listed in Appendix 1. The prepared knowns had the means and standard deviations (each analyst-day has $n = 3$) shown in Table I.

TABLE I			
MEANS AND STANDARD DEVIATIONS FOR KNOWNs			
	Analyst N	Analyst S	Total
Day 1	-0.00037 ± 0.0014	0.0041 ± 0.0031	-0.0023 ± 0.0030
Day 2	-0.0029 ± 0.0024	-0.0029 ± 0.0031	-0.0029 ± 0.0024
Grand Total	-0.0016 ± 0.0022	-0.0035 ± 0.0029	-0.0026 ± 0.0026 n = 12

There is a significant bias in the Grand Total for Analyst S, primarily because of the results of the Day 1 knowns. The Day 2 Totals and the Grand Total also indicate a significant negative bias in the knowns data. The only individual analyst-day combination with a statistically significant bias is Analyst S-Day 1 combination.

Blinds

Each analyst titrated 13 blind standards. The results of the individual analyses are listed in Appendix 1. Two outliers, both generated by Analyst S, were removed from the high precision titration blinds data. Thus n=13 for Analyst N and n = 11 for Analyst S. After removing the outliers, the range of RD% for the blinds is from -0.014 to +0.0039. All but the three lowest blinds are within the established NBL limits for the high precision titration. The three negative blinds outside these limits were generated by Analyst N who had only one positive RD% in the two days of blinds measurements.

The high precision titration blinds had RD%s with the means and standard deviations shown in Table II.

TABLE II			
MEANS AND STANDARD DEVIATIONS OF BLINDS			
	Analyst N	Analyst S	Total
Day 1	-0.0033 ± 0.0039 n = 6	-0.0032 ± 0.0055 n = 6	-0.0033 ± 0.0045 n = 12
Day 2	-0.0064 ± 0.0044 n = 7	+0.00099 ± 0.0023 n = 5	-0.0033 ± 0.0052 n = 12
Grand Total	-0.0050 ± 0.0043 n = 13	-0.0013 ± 0.0047 n = 11	-0.0033 ± 0.0048 n = 24

The negative bias in the data reported by Analyst N is statistically significant. Also of interest is that the results of the blinds as measured by Analyst N generally are lower than the results of the knowns, whereas the opposite occurs in the data reported by Analyst S whose results of blinds generally are higher than those of the knowns. The differences between knowns and blinds are not significant.

Results from the combined knowns and blinds are similar; both indicate nearly the same negative bias. The means with 95% confidence interval are

-0.0033 ± 0.0020 for the blinds with n = 24
-0.0026 ± 0.0017 for the knowns with n = 12

Table III shows the results of the variance component analysis and the analysis on which the NBL Laboratory Limits were based.

TABLE III					
LABORATORY LIMITS ESTABLISHED BY VARIANCE COMPONENT ANALYSIS					
	Systematic Error: Mean RD	Analyst Variation	Analytical Variation (Random)	Total Random Variation	Random + Systematic Error
Current Lab Limits	-0.00044	0.0017	0.0036	0.0043	0.0047
Laboratory Limits: 0.009			Extremes: 0.013		
"Knowns"	-0.0026	0.0008	0.0026	0.0027	0.0053
"Blinds"	-0.0033	0.0027	0.0046	0.0053	0.0086
Recommended Limits for Blinds Laboratory Limits: 0.017			Extremes: 0.026		

High precision laboratory limits (laboratory basis) were based on the historical values of knowns of work completed during FY 91 (n = 39); the total random variation in the laboratory basis data also included a component of variation due to period.

The "knowns" and the "blinds" data exhibit a significant bias that was not found in the original Laboratory basis data. However, the total errors (the sums of the random and systematic errors) are similar in the two sets. Note that there is a decrease in the amount of random variation in the new data. In the original data,

the random variation outweighs the systematic variation by almost an order of magnitude, while in the newer data the random and systematic contributions to total variation are almost equal.

The total error may be considered to be the standard deviation of the method. Thus the limits established (two times the total error) are at the 95% level of confidence and the extremes are approximately the 99% level of confidence (approximately three times the total error).

REFERENCES

1. NBL Quality Assurance Manual, p. 28, November 1990.
2. "Determination of Uranium by the High-Precision Titrimetric Method - Gravimetric Version," NBL-SA-U(E)-2.2, NBL Procedures Manual.
3. "Blinds for High Precision Method," Final Internal Project Report, 1993.

APPENDIX 1				
HPT METHOD RESULTS FOR 2.5-TO 3.5-GRAM KNOWNs				
Analyst	%U Found	%RD*	Day	Date
N	99.9762	0.0012	1	09/10/92
N	99.9735	-0.0015	1	09/10/92
N	99.9742	-0.0008	1	09/10/92
N	99.9744	-0.0006	2	11/13/92
N	99.9697	-0.0053	2	11/13/92
N	99.9722	-0.0028	2	11/13/92
S	99.9722	-0.0028	1	09/22/92
S	99.9731	-0.0019	1	09/22/92
S	99.9673	-0.0077	1	09/22/92
S	99.9752	0.0002	2	09/30/92
S	99.9721	-0.0029	2	09/30/92
S	99.9691	-0.0059	2	09/30/92
Mean RD = - 0.0026% Std. Dev. = 0.0026% n = 12				

$$* \%RD = \frac{\text{titrated value} - \text{certified value}}{\text{certified value}} \times 100$$

APPENDIX 2				
HPT METHOD RESULTS FOR 2.5- TO 3.1-GRAM BLINDS				
Analyst	%U Found	%RD*	Day	Date
N	99.9650	-0.0100	1	09/10/92
N	99.9750	-0.0000	1	09/10/92
N	99.9730	-0.0020	1	09/10/92
N	99.9697	-0.0053	1	09/10/92
N	99.9724	-0.0026	1	09/10/92
N	99.9744	-0.0006	1	09/10/92
N	99.9698	-0.0052	2	11/13/92
N	99.9611	-0.014	2	11/13/92
N	99.9716	-0.0034	2	11/13/92
N	99.9631	-0.012	2	11/13/92
N	99.9703	-0.0047	2	11/13/92
N	99.9714	-0.0036	2	11/13/92
N	99.9721	-0.0029	2	11/13/92
S	99.9680	-0.0070	1	09/22/92
S	99.9220	-0.053**	1	09/22/92
S	99.9730	-0.0020	1	09/22/92
S	99.9668	-0.0082	1	09/22/92
S	99.9786	+0.0036	1	09/22/92
S	99.9664	-0.0086	1	09/22/92
S	99.9773	+0.0023	1	09/22/92
S	99.9544	-0.021**	2	09/30/92
S	99.9737	-0.0013	2	09/30/92
S	99.9763	+0.0013	2	09/30/92
S	99.9788	+0.0038	2	09/30/92
S	99.9774	+0.0024	2	09/30/92
S	99.9740	-0.0010	2	09/30/92
Mean RD = -0.0033%				
Std. Dev. = 0.0048%				
n = 24				

** Outliers, excluded from HPT blinds data

REFERENCE MATERIALS PROGRAM

P. M. Santoliquido and J. B. Jeans

A primary responsibility of NBL to the DOE Safeguards Program is to provide nuclear reference materials to insure that safeguards measurements meet essential compatibility, reliability, and traceability to the national measurement base as mandated by DOE. During FY 93, 59 different certified reference materials (CRMs) were available for sale. Of these, 42 CRMs had sales ranging from 1 to 112 units. A listing of FY 93 sales by CRM is given in Table I. Purchasers of CRMs represented 48 separate organizations including 7 U. S. DOE contractors, 14 U. S. Nuclear Regulatory Commission (NRC) licensees, 7 U. S. academic institutions, 5 other U. S. customers, and 15 facilities in 15 foreign countries. A total of 88 orders (33 foreign and 55 domestic) for 538 units (318 foreign and 220 domestic) valued at \$171,625 was shipped. Figure 1 shows market shares of sales for FY 93 and each of the prior three years.

The 1989 certification of the National Institute of Standards and Technology (NIST) Standard Reference Material, Potassium Dichromate (SRM 136e), a widely used nuclear applications oxidimetric reference material, was a cooperative effort of NIST and NBL. During FY 93 at NIST's request, NBL participated and completed its work on a stability study of this reference material (See "A Stability Check on SRM 136e Potassium Dichromate" in this document).

The work on CRM 124(1-7), U_3O_8 with twenty-four impurity elements, was completed, and the final certificate of analysis is to be issued in FY 94. When copies are received from the printer, they will be distributed to purchasers of record.

During this reporting period, progress was made on the preparation and certification of CRM 144 which contains ^{240}Pu , ^{242}Pu , ^{244}Pu . This triple-atom plutonium isotopic material is intended for use as a combined internal isotopic standard and assay spike for mass spectrometric analysis. Unit production, elaboration of a statistical plan, and mass spectrometric measurements were completed. The remaining tasks: coulometric assays, final calculations, statistical review of the data, drafting of the certificate, and development of the costing data will be completed in FY 94.

Material for CRM 139, neptunium oxide, was processed at Los Alamos National laboratory (LANL). However, a review of changing needs and priorities for DOE-supported reference materials resulted in this project being put on hold and in the material being placed in storage.

Material was also processed at LANL for plutonium oxide isotopic CRMs for mass spectrometry. Four enrichments were prepared as follows: CRM 140, 98% ^{239}Pu ; CRM 141, 90% ^{239}Pu ; CRM 142, 75% ^{239}Pu ; and CRM 143, 50% ^{239}Pu . Work planned for FY 94 includes preliminary characterization by LANL, acceptance of the material by NBL, transportation of the material to NBL, unit packaging at NBL, and start of the certification work. Completion of the certification work in FY 95 is planned. CRMs 140-143 were designed to replace the plutonium sulfate isotopic CRMs issued by the National Bureau of Standards (NBS now NIST) in 1970.

Efforts to address the lack of CRMs for nondestructive analysis are proceeding along two lines. The first is the preparation of a document intended to facilitate better measurement control through improved traceability. Preparation of this document is nearing completion, and publication as an NBL topical report is scheduled for early FY 94. The second line of endeavor is to assist the members of the calorimetry exchange group in the preparation and documentation of measurement control standards for calorimetry. This second project will begin in FY 94.

A new edition of the NBL Certified Reference Materials Catalog is in preparation and will be distributed in 1994.

FY 93 SALES BY CRM					
TABLE I					
RANK	CRM	DESCRIPTION	UNITS SOLD		
			FOREIGN	DOMESTIC	TOTAL
1	129	U_3O_8 ASSAY	69	43	112
2	124(1-7)	U_3O_8 IMPURITIES	49	5	54
3	U030-A	U ISOTOPIC, 3%	34	10	44
4	U050	U ISOTOPIC, 5%	24	17	41
5	U005-A	U ISOTOPIC, 0.5%	25	14	39
6	66(1-7)	TH OXIDE IMPURITIES	3	25	28
7	112-A	NORMAL U METAL	21	5	26
8	U010	U ISOTOPIC, 1%	22	2	24

FY 93 SALES BY CRM (Continued)

TABLE I

			UNITS SOLD		
RANK	CRM	DESCRIPTION	FOREIGN	DOMESTIC	TOTAL
10	U500	U ISOTOPIC, 50%	13	1	14
11	123(1-7)	U ₃ O ₈ IMPURITIES	0	12	12
12	105-A	PITCHBLEND-SILICA	3	7	10
13	U020-A	U ISOTOPIC, 2%	10	0	10
14	111-A	²³³ U SPIKE	5	5	10
15	103-A	PITCHBLEND-SILICA	2	7	9
16	U970	U ISOTOPIC, 97%	1	7	8
17	18	UO ₃	1	6	7
18	106-A	MONAZITE-SILICA	5	1	6
19	135	²³⁵ U SPIKE	2	4	6
20	130	²⁴² Pu SPIKE	0	6	6
21	101-A	PITCHBLEND-SILICA	5	0	5
22	U00002	U ISOTOPIC, 0.02%	1	4	5
23	104-A	PITCHBLEND-SILICA	4	0	4
24	109-A	MONAZITE-SILICA	4	0	4
25	115	DEPLETED U METAL	1	3	4
26	U015	U ISOTOPIC, 1.5%	4	0	4
27	102-A	PITCHBLEND-SILICA	3	0	3
28	107-A	MONAZITE-SILICA	3	0	3
29	118	BISO BEADS	0	3	3
30	119	TRISO BEADS	0	3	3
31	U930	U ISOTOPIC, 93%	0	3	3
32	108-A	MONAZITE-SILICA	2	0	2
33	U900	U ISOTOPIC, 90%	0	2	2

FY 93 SALES BY CRM (Continued)

TABLE I

			UNITS SOLD		
RANK	CRM	DESCRIPTION	FOREIGN	DOMESTIC	TOTAL
34	42(1-4)	PITCHBLEND-SILICA	0	1	1
36	117	U ISOTOPE MIXTURE	0	1	1
37	125	UO ₂ PELLETS	0	1	1
38	126	PLUTONIUM METAL	0	1	1
39	131	²⁴⁴ Pu SPIKE	0	1	1
40	969	U GAMMA SPEC	0	1	1
41	U150	U ISOTOPIC, 15%	0	1	1
41	U200	U ISOTOPIC, 20%	0	1	1

NBL REFERENCE MATERIAL SALES Market Shares FY 1990 - FY 1993

Figure 1

A STABILITY CHECK ON SRM 136e POTASSIUM DICHROMATE

W. Nichiporuk

Introduction

The 1989 certification of Standard Reference Material (SRM) 136e Potassium Dichromate, a widely used nuclear applications oxidimetric reference material, was a cooperative effort of the National Institute of Standards and Technology (NIST) and NBL.

The certified oxidimetric assay value of 99.984 ± 0.010 Wt.% for the material is a weighted mean of results from three different analytical assays:¹ the coulometric analysis, the gravimetric titration, and the high-precision version of the NBL-modified titrimetric method for uranium. NBL certified reference material (CRM) 112-A (formerly SRM 960), Uranium Metal Standard, was used at NBL in the analysis of ten bottles of SRM 136e in duplicate or triplicate along with samples of CRM 99 (NBL Potassium Dichromate Standard) and SRM 136c (a previous lot of the NIST Potassium Dichromate Standard) which were used as controls.

In the NIST Certificate of Analysis, dated June 1, 1989, the SRM 136e is described as a stable oxidimetric standard with certificate validity extending over a period of five years, provided the material has been stored in its original container with the top tightly closed.

At the end of 1992, when NIST was about to perform a stability check of SRM 136e, NIST requested that NBL once again do the high precision titrimetric work on the material to supplement the coulometry assay that NIST would be doing. It was important to NIST that the same NBL analyst who did the previous certification work also do the stability check. No statistical support from NBL was necessary, because NIST was to handle all data evaluation. Therefore, only individual, raw sample results would be reported and compared to the 1989 certificate value.

In addition NBL and NIST agreed that for the purposes of the stability check, the same plan that the two organizations used for the 1989 certification would be adopted in which both dried and undried potassium dichromate was used.

At NBL, the cooperative measurement effort was coordinated through the Reference Materials Program Office, which also provided an outline of the applicable sampling procedure along with a sequence in which samples (SRM 136e)¹ and controls (CRM 99)² were to be titrated.

Sampling and Analysis

Approximately four grams of material were taken from each of four 50-g storage bottles of SRM 136e Potassium Dichromate, which were sent by NIST, labeled A through D. The samples were dried to constant weight in Pyrex™ weighing bottles at 110°C, and the percent loss-on-drying was calculated.

Upon completion of the drying measurements, subsamples of the dried material were taken from three (A through C) of the weighing bottles and analyzed for the oxidimetric assay value. Concurrently, subsamples of the undried material from the same sample bottles as well as control samples of CRM 99 were analyzed according to the sequence shown below. The analysis method was the high precision titration against CRM 112-A, Normal Uranium Metal.³

Samples and Controls Titration Sequence

(all analyses performed in one day)

CRM 99 (undried)
SRM 136e, Bottle A (undried)
SRM 136e, Bottle A (dried)
CRM 99 (undried)
SRM 136e, Bottle B (dried)
SRM 136e, Bottle B (undried)
CRM 99 (undried)
SRM 136e, Bottle C (undried)
SRM 136e, Bottle C (dried)
CRM 99 (dried)

Results

Loss-on-drying measurements on four SRM 136e samples are listed in Table I. Oxidimetric assay measurements on six SRM 136e samples are listed in Table II. Similar measurements on four control samples of CRM 99 are also listed. For comparison, Table II includes the certificate values for the two dichromates.

TABLE I				
SRM 136E POTASSIUM DICHROMATE/LOSS-ON-DRYING MEASUREMENTS				
Description	Bottle A	Bottle B	Bottle C	Bottle D
Sample wt. before drying, g	4.12147	4.25157	4.11756	4.03865
Sample wt. after drying, g	4.12130	4.25149	4.11750	4.03856
Loss-on-drying, g	0.00017	0.00008	0.00006	0.00009
Loss-on-drying, wt. %	0.0041	0.0019	0.0014	0.0022

TABLE II			
HIGH PRECISION TITRIMETRIC ANALYSIS OF CSRM 136E AND CRM 99			
POTASSIUM DICHROMATES			
NBL/NIST No.	Bottle No.	U Metal Titrated, g	Oxidimetric Assay, Wt. %
			CRM 99 SRM 136e
CRM 99	10	3.48090	99.9687 (undried)
SRM 136e	A	3.25877	99.9884 (undried)
SRM 136e	A	3.36377	99.9776 (dried)
CRM 99	45	3.61553	99.9853 (undried)
SRM 136e	B	2.45017	99.9913 (dried)
SRM 136e	B	3.60781	99.9817 (undried)
CRM 99	76	3.38658	99.9787 (undried)
SRM 136e	C	2.74824	99.9831 (undried)

TABLE II (Continued)			
HIGH PRECISION TITRIMETRIC ANALYSIS OF CSRM 136E AND CRM 99			
POTASSIUM DICHROMATES			
NBL/NIST No.	Bottle No.	U Metal Titrated, g	Oxidimetric Assay, Wt. %
			CRM 99 SRM 136e
CRM 99	84	2.56451	99.9825 (undried)
Results Summary		Means Wt. %	99.979
		Std. Dev.	0.007
Certificate Values		Means Wt. %	99.977
		Std. Dev.	0.006
		Dates of Certificates	(07/15/88)
			99.986
			0.006
			99.984
			0.010
			(06/01/89)

Table II indicates that the differences between the present mean oxidimetric assays of the SRM 136e and CRM 99 Potassium Dichromates, and their certification assays as established four or five years ago, are very small and fully within the standard deviation limits of the past and present assays.

A formal statement concerning stability of the two potassium dichromates with time, especially the stability of the SRM 136e dichromate, must await completion of the coulometric assay of SRM 136e by NIST as well as NIST's statistical evaluation of the NBL and NIST results.

REFERENCES

1. Certificate of Analysis, CRM 99 Potassium Dichromate, Oxidimetric Standard, New Brunswick Laboratory, Argonne, IL, July 15, 1988.
2. Certificate of Analysis, Standard Reference Material 136e, Potassium Dichromate, Oxidimetric Standard, Gaithersburg, MD, June 1, 1989.
3. "Determination of Uranium by the NBL High Precision Titrimetric Method-Gravimetric Version," NBL-SA-U(E)-2.2, NBL Procedure Manual.

MEASUREMENT SERVICES PROGRAM

A. V. Stiffin and R. D. Oldham

NBL, as the Government's Nuclear Material Measurement and Standards Laboratory, supports the nuclear safeguards programs by providing independent measurements on a variety of nuclear materials. NBL serves

as an arm of OSS and provides services on a contractual basis to the NRC. During FY 93, NBL received 112 uranium samples for analysis. A wide variety of analyses, such as titrimetry, gamma spectrometry, and mass spectrometry were performed on these samples.

NBL provided assistance to the DOE Anomaly Resolution Team (DART) by analyzing 19 uranium samples. These samples were dissolved, analyzed and reported in the shortest time period ever accomplished at NBL for a group of samples of this type. The average measurement uncertainty on the uranium assays was calculated to be better than 0.02% RSD and better than 0.003% RSD for the isotopic analyses. NBL also provided assistance to Y-12 by analyzing six uranyl nitrate solution samples to resolve a shipper/receiver difference and to the Idaho Chemical Processing Plant (ICPP) by characterizing three UO_3 working standards.

The NRC Office of Nuclear Materials Safety and Safeguards (NRC/NMSS) submitted a total of 61 uranium samples for materials verification under the Nuclear Materials Safeguards Program. These samples included pure product materials such as UO_2 powders and pellets, complex fuel materials, impure materials such as grinder sludges, incinerator and calcined ashes, and liquid samples such as uranyl nitrate hexahydrate solutions and discard tank samples.

The NRC contract with NBL, administered under the Measurement Services Program, also provides technical support and assistance. NBL provided technical support to the NRC Physical Security MC&A Licensing Inspection Section by assisting NRC inspectors during inspections at General Electric (GE) in Wilmington, NC (March, 1993), Babcock and Wilcox (B&W) in Lynchburg, VA (May, 1993), Siemens Nuclear Power Corporation (July, 1993), and Westinghouse CFFF (September, 1993). NBL helped evaluate the effectiveness of the licensees' special nuclear measurement systems and control programs to verify compliance with 10 CFR 74.31, 74.51, or 75.1, and helped collect samples for inventory verification.

Finally, there were 23 uranium samples received as part of NBL's participation in sample exchange programs. They consisted of 17 uranyl nitrate samples, two uranium-contaminated alumina samples, two UF_6 samples, and two UO_3 samples received from the NBL Safeguards Measurement Evaluation (SME) Program. NBL participates in the SME Program not only to meet requirements for participation in a samples exchange program, but also to evaluate the stability and integrity of sample materials in the program.

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