NBL-304

PROGRESS REPORT FOR THE PERIOD OCTOBER 1980 THROUGH SEPTEMBER 1981

March 1982

U. S. DEPARTMENT OF ENERGY
CHICAGO OPERATIONS OFFICE
NEW BRUNSWICK LABORATORY
ARGONNE, ILLINOIS

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PROGRESS REPORT FOR THE PERIOD OCTOBER 1980 THROUGH SEPTEMBER 1981

DOE RESEARCH AND DEVELOPMENT REPORT

NEW BRUNSWICK LABORATORY

CHICAGO OPERATIONS OFFICE

CARLETON D. BINGHAM, DIRECTOR

MARCH 1982

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NOTICE

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SUMMARY

This report describes the technical activities of the New Brunswick Laboratory performed during FY 1981 in support of its mission as the U.S. Government's Nuclear Materials Standards and Measurement Laboratory.

Studies with a modified coulometric titration have resolved the negative bias previously found when determining greater than 40-mg quantities of uranium with the Lawrence Livermore National Laboratory Automated Titrator. This titration system is currently capable of determining uranium with an unbiased measurement uncertainty within ± 0.05% (relative).

High measurement titration results using the NBL modified uranium titration method and frequent electrode malfunctioning were traced to the quality of the phosphoric acid reagent used. The problem was solved with the development of a satisfactory electrode cleanup method and by careful test selection of phosphoric acid from various suppliers.

Since a precision of 0.02% relative standard deviation (RSD) for the NBL modified uranium titration recently had been achieved under ideal conditions, a study was initiated to determine the causes of any subsequent changes in accuracy that might be evident at this improved level of precision. Several important observations were made but further work is needed to confirm the results and to draw conclusions from these tests.

An accurate technique has been developed to determine uranium isotopic values nondestructively in small samples by comparing the 89-keV X-ray peak from ^{235}U decay with a 92-keV gamma-ray doublet from a ^{238}U daughter. Results show an average absolute difference between accepted and measured values of less than 0.3% over an enrichment range of 0.3 to 60% ^{235}U. This technique has excellent application possibilities for safeguards inspectors.

An interlaboratory comparison was concluded for the evaluation of a method proposed for consideration by the American Society for Testing and Materials for the determination of plutonium in plutonium dioxide using controlled-potential coulometry. Repeatability and reproducibility values

were larger than expected. Because it was not a requirement of the test protocol to correct the assay values of the plutonium dioxide test material for systematic errors derived from the measurement of standards made during the same day, a large between-laboratory component of variance was observed. However, pooled results from four of the five laboratories showed excellent agreement (-0.004% relative difference) between the interlaboratory mean and the assigned value of the plutonium test material.

The suitability of an EG&G PAR Model 173/179 controlled-potential coulometer was evaluated for use with the NBL coulometric method for the determination of plutonium as a replacement for the existing MT Model 3 coulometer which is no longer commerically available. Test results show that, although the precision for the EG&G PAR (0.05% RSD) is comparable to that for the MT instrument (0.03% RSD), the linearity of the EG&G PAR unit over the working current range of 0.01 to 50 mA is dramatically poorer resulting in a systematic error of 0.13% in the determination of plutonium.

Three alternative end point determination techniques (predictive, arbitrary time cut-off, and arbitrary current cut-off) widely used in controlled-potential coulometric methods for plutonium determination were compared to the NBL control-potential-adjustment technique. Unbiased results were obtained with both cut-off techniques when chemical calibration was used but the precision of the time cut-off method was poor (0.2% RSD). When electrical calibration of the coulometer was used, the cut-off techniques gave results biased low by 0.1-0.2% while only the predictive end point gave a precision and accuracy comparable to the NBL technique.

A Los Alamos National Laboratory ion-exchange method for separating trace amounts of uranium from plutonium has been evaluated and preliminary results on two plutonium metal samples, in which the separated uranium was determined by laser fluorometry, are in agreement with the interlaboratory mean from the Plutonium Metals Exchange Program.

A solid-state, low-voltage field control magnet system was installed on a 30-cm radius, 90-degree magnet sector surface ionization mass spectrometer in an effort to minimize operating problems and instrument downtime. The new system, under total programmable calculator control, has been shown to be reliable and to provide satisfactory reproducibility of uranium isotopic values.

Since the mass discrimination in uranium standards is being applied to plutonium isotopic measurements made by surface ionization mass spectrometry until satisfactory plutonium standards are available, the mass discrimination factor for plutonium relative to that of uranium was studied using calibrated or certified solutions of both elements. Results show that the fractionation and mass discrimination corrections for uranium and plutonium are sufficiently similar to allow the continued interim use of uranium standards for plutonium measurements.

The resolution, sensitivity, and portability of the plasma-desorption mass spectrometer used to determine the isotopic composition of untreated solid uranium samples has been enhanced by the use of a ^{252}Cf source and by the addition of microchannel plate ion and fission fragment detectors.

During FY 1981, 866 NBL certified reference material (CRM) units were sold to a total of 43 USA and non-USA customers, the most popular for safeguards purposes being UO_2 (CRM No. 97), U_3O_8 (CRM Nos. 98 and 114), and UF_6 (CRM No. 113). Uranium dioxide pellets are being certified as an NBL reference material (CRM No. 125) for uranium assay and isotopic composition. Impurity determinations are in progress for the certification of NBL CRM No. 121, UO_2, as a uranium spectrographic impurity reference material. Because of an unexpected exceptionally high demand for NBL CRM No. 98, U_3O_8, NBL inventories have been rapidly depleted and are currently exhausted, necessitating an accelerated replacement schedule. (Work is in progress to replace CRM No. 98 with two reference materials, CRM Nos. 123 and 124, which will extend the usefulness of the materials and conserve inventory life.) High-fired (1600°C) UO_2 beads are being evaluated for use as reference material for uranium assay and isotopic measurement because of their apparent superior resistance to moisture degradation. The certification of five low-level uranium counting standards (NBL CRM Nos. 101-A through 105-A) has been completed. The certification of three prototype non-destructive assay reference materials (ion-exchange resin, cellulose fiber, and synthetic calcined ash) has been completed. Two complex uranium reference solutions were prepared and certified for the Nuclear Regulatory Commission as part of their safeguards evaluation of the measurement capabilities of licensed nuclear fuel facilities. A 1982 edition of the NBL Certified Reference Material Catalog has been prepared for publication.

Under an Interagency Agreement between the Department of Commerce and the Department of Energy, the National Bureau of Standards (NBS) has transferred all Special Nuclear Material Standard Reference Materials (SRM) to NBL for distribution. NBL will prepare and certify new replacement materials for existing NBS SRMs for issuance as NBL CRMs except in cases involving unique technical considerations.

The Safeguards Analytical Laboratory Evaluation (SALE) Program consisting of 49 active participants (27 USA, 22 non-USA) continues to function satisfactorily. An annual report was issued which summarized and evaluated all data received during the 1980 calendar year. The SALE Steering Committee recommended that scrap/waste materials be included in the program and that more definitive statements be made about method capabilities. The Fourth SALE Program Participants Meeting was held during July, 1981, and minutes of the meeting were compiled for distribution. All sample shipments scheduled for FY 1981 were made, with the exception of plutonium shipments to Japan and Czechoslovakia, and arrangements are being made to resolve these cases. In addition to the four materials currently distributed in the program, preparations are being made for the inclusion of high-fired (1250°C) plutonium oxide powder, and uranium dioxide pellets.

The General Analytical Evaluation (GAE) Program, directed at the evaluation of measurement performance on input material for enriched scrap recovery operations, continued at a satisfactory level with seven participants. Recommendations were made by the participants to include an impure U_3O_8 material for assay, a material with less than 5% ^{235}U enrichment, and uranium oxide samples with low impurity levels for analysis.

The measurement phase of the NBL Nondestructive Assay Reference Materials Program for the evaluation of the measurement capabilities of participating laboratories for scrap and waste materials has continued. Of the 18 organizations participating, the twelfth participant was in the process of measuring these materials.

The Los Alamos National Laboratory L_{III}-edge densitometer has been under evaluation to fully define its operating parameters and scope of application. At the end of FY 1981, the study was nearly complete with L_{III}-edge measurements and chemical analyses concluded on uranium, plutonium, and uranium-plutonium synthetic test solutions.

Seventeen journal articles, topical reports, and presentations were authored by seventeen NBL staff members during FY 1981. One patent was awarded.

I. INTRODUCTION

The DOE New Brunswick Laboratory (NBL) is the U.S. Government's Nuclear Materials Standards and Measurement Laboratory. NBL is assigned the mission to provide and maintain, as an essential part of federal statutory responsibilities related to national and international safeguards of nuclear materials for U.S.A. defense and energy programs, an ongoing capability for: the development, preparation, certification, and distribution of reference materials for the calibration and standardization of nuclear materials measurements; the development, improvement, and evaluation of nuclear materials measurement technology; the assessment and evaluation of the practice and application of nuclear materials measurement technology; expert and reliable specialized nuclear materials measurement services for the government; and technology exchange and training in nuclear materials measurement and standards. This report highlights and summarizes the technical activities of NBL during FY 1981 in fulfilling its assigned mission.

II. THE DEVELOPMENT OR EVALUATION OF MEASUREMENT TECHNOLOGY

A. ELEMENTAL ASSAY

1. URANIUM

1.1 Application of a Modified Coulometric Titration Method to the LLNL Automated Titrator (W. G. Mitchell and K. Lewis) A manually-controlled, coulometric titration of uranium using a modified end point approach with appropriate time restraints was previously used to titrate 40-140 mg U with an accuracy of ± 0.05% and a precision of 0.05% relative standard deviation (RSD) or better.[1] This study was made in an attempt to resolve the bias previously encountered in the Lawrence Livermore National Laboratory (LLNL) Automated Titrator.[2] During the current report period the implementation of the modified coulometric titration method into the LLNL Automated Titration System required the following: (1) restoration of mechanical operation of the system; (2) changes in the computer program to automate the modified titration method; and (3) verification of the success of the modified titration method in removing the bias in the LLNL Automated Titrator.

Inoperative parts of the autotitration system were restored to full mechanical use. The chronic malfunctioning of the reagent flow switches was circumvented through computer changes to eliminate their fault control off-switching. Once the system was operating, titrations were carried out with the original autotitration method. The same biased results for more than 40 mg U were obtained as had been previously found.

To introduce the exact modified coulometric titration method developed with the manual titration system[1,3] would have required a total rewrite of the FOCAL control program of the autotitrator's computer. Therefore, it was decided to introduce only those elements of the modified method determined to be critical in obtaining accurate and precise results over the range of 40-140 mg U. The elements changed were: (1) indicator potential control of the titration replaced a previously used titration curve slope control; (2) a high titration current of 400 mA replaced the 300 mA current to remain within the time constraints of the method; and (3) pulsing of the high current in the region at the foot of the titration curve was introduced. These changes altered the titration method but allowed retention of major sections of the FOCAL control program which carried out system control and mathematical manipulation of data.

Preliminary titration data obtained using the modified FOCAL control program in the autotitration system for 40-140 mg U gave a precision of 0.05% or better and accuracies of +0.02 to -0.07%. At that time, malfunctions caused a system shutdown. Reexamination of the system showed inaccuracies throughout the 40 to 140-mg U range; such full range inaccuracies had not been previously found. Studies with the manual coulometric system pointed to problems with the phosphoric acid.[4] Similar problems with the phosphoric acid were noted concurrently by analysts at NBL using the manual titrimetric procedure for uranium.

When acceptable phosphoric acid became available, the study of the autotitrator continued. A random titration series with a total of 72 titrations (24 each at 40, 100, and 140 mg U) was carried out. The overall accuracy was +0.003% with a precision of 0.084% (RSD). The accuracy at each uranium level titrated was within 0.05%. The precision at the 40-mg U level was initially poorer than 0.05% RSD, but changing the treatment of the indicator electrode gave the desired precision control. Another random titration series with a total of 36 titrations (12 each at 40, 100, and 140 mg U) gave an accuracy within 0.05% and a precision of 0.05% (RSD). Titrations of 20 mg U have also been successful using the FOCAL program modifications and introducing a second high generation current (150 mA) for these smaller amounts of uranium.

The random titration series on standard uranium solutions with the automated system have supported the effectiveness of the modified coulometric method in eliminating the bias previously found. Titrations of samples commonly received at NBL are to be carried out on the autotitrator using the modified FOCAL program. If the sample titration results support the standard titration results, the autotitrator should be available for routine sample analyses within the laboratory.

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1. W. G. Mitchell and K. Lewis, NBL-297 (1981), pp. 1-3.

2. K. Lewis, NBL-294 (1980).

3. W. G. Mitchell and K. Lewis, NBS Sp. Pub. 582 (1980), pp. 140-146.

4. W. G. Mitchell and M. Werle, NBL-304 (1982), p. 3.

1.2 <u>Study of the Effects of Various Phosphoric Acids on the Titration of Uranium</u> (W. G. Mitchell and M. D. Werle) Certain production lots of Mallinckrodt Chemical Works (Mallinckrodt) phosphoric acid, when treated at this laboratory with 2% $K_2Cr_2O_7$ for use in uranium titrations, gave a green color rather than the normal straw color upon standing. Concurrently, a problem with high titration results was found during sample analyses with the NBL-modified titration of uranium.[1] Results were 0.05-0.62% high with values increasing throughout the day. Fusion of the platinum indicator electrode in $NaHSO_4$, followed by the normal electrode treatment of flaming and quenching in HNO_3 was able to eliminate the high results for only one or two titrations before the problem returned. Erratic titration results also occurred at the same time with the LLNL Automated Titrator, a coulometric titrator for uranium being studied at NBL which uses electrogeneration of titrant at a gold electrode. To define the problem with the coulometric titrations, a manually-controlled coulometric titration apparatus described previously[2] was used. Results indicated that problems with the coulometric titration stemmed from new lots of phosphoric acid. These problems could not be eliminated for even one or two titrations by fusion and cleaning of the indicator electrode alone since the gold generator electrode was also affected.

Further study of the coulometric titration system showed there was a complex interaction resulting from the apparent "poisoning" of the gold generator electrode. Several chemical methods were used to clean the surface of the electrode, but failed as long-term solutions as the surface became contaminated again apparently by diffusion of the "poison" from within the gold. Furthermore, during titrations some of the "poison" from the gold generator electrode could become deposited on the platinum indicator electrode so that a previously cleaned platinum indicator electrode could be poisoned again from the gold generator electrode even in "clean" H_3PO_4. Thus a cleanup procedure for the gold generator electrode used with the new lots of H_3PO_4 was required. An electrochemical method was devised in which the electrode was placed in a titration blank and a 5-mA current was passed between the gold electrode and a platinum counter electrode for four hours with a large platinum electrode present in the solution. Results from titrations in "clean" H_3PO_4, shown in Table I, indicate the long term success of the electrochemical cleaning.

TABLE I

Comparative Long-Term Coulometric Uranium Titration Results after Chemical and Electrochemical Gold Electrode Cleanup

Method	Deviation from Reference Value, % After one day	 After two weeks	 After five-six weeks
Chemical[(a)]	+0.005	+0.110	+0.139
Electrochemical	+0.009	+0.022	+0.015

(a) Best chemical cleanup found was fusion in $NaHSO_4$, burnishing, and treatment with hot HCl.

There have been indications in other electrochemical work[3,4] that purification of H_3PO_4 was required for some work with platinum electrodes because of the presence of H_3PO_3 in the H_3PO_4. A qualitative test[5] of several lots of Mallinckrodt H_3PO_4 showed the presence of reducing substances in those lots which had caused problems. No specific poisoning agent in the Mallinckrodt H_3PO_4 could be identified by emission spectrographic analyses of a copper column used to separate the metals from the acid and a sulfide precipitate of the heavy metals from the acid, nor by X-ray fluorescence analysis of the poisoned gold generator electrode. Additional extensive work would be necessary to identify the electrode poison.

As an expediency in resolving the poisoning effect, phosphoric acid available from other manufacturers was tested for applicability in both titration systems. J. T. Baker Chemical Company (Baker) and Fisher Scientific Company (Fisher) reagent-grade phosphoric acids were evaluated and found to cause polarization of the gold generator electrode in the coulometric titration system probably from the effect of impurities as previously reported.[6] Ultimately Baker and Matheson, Coleman, and Bell (MCB) H_3PO_4 were found satisfactory for the NBL modified titration, but only MCB was suitable for the coulometric LLNL Automated Titrator.

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4. J. Bravacos, M. Bonnemay, E. Levart, and A. A. Pilla, C. R., Acad. Sc. Paris C265, 337 (1967).

5. ACS Specifications of Reagent Chemicals and Standards, 4th Ed., (American Chemical Society, Washington D.C., 1968), pp. 346-347.

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1.3 Chemical Reactions of the NBL Titration - A Progress Report

(B. W. Moran) The NBL titrimetric determination of uranium was previously demonstrated to be "rugged" to procedural variations of ±10%.[1,2] Recently the precision of the method was improved and routine precisions of 0.02% RSD were achieved under ideal conditions when the established procedure was strictly followed and all reagents and apparatus were equilibrated at 25°C. The present work attempted to determine the causes of any changes in accuracy that might occur at this improved level of precision and to determine if procedural modifications might further enhance the method.

The reactions of the NBL titration were followed using spectrophotometric, voltammetric, and potentiometric techniques. Trace quantities of Fe(II) and Mo(V) could not be measured in the solution matrix by spectrophotometry. Potentiometry was used to follow the progress of reactions to determine when equilibrium had been reached or a reaction had been completed. Fast sweep voltammetry was used to qualitatively identify some of the ionic species present. Potentiometry and voltammetry were used simultaneously or separately on tested solutions.

The chemistry of the NBL titration is dependent upon changes in oxidation-reduction potentials and equilibria with changes in temperature and acid concentrations,[4] especially that of H_3PO_4.[2] The potentials of all metallic ion couples used in the procedure (Cr, Fe, Mo, U, V) are significantly affected by H_3PO_4 concentration; all the potentials became more oxidizing with increased H_3PO_4 concentration except that of iron which becomes more reducing.

The reduction reaction is rapid and establishes an equilibrium potential within 15 seconds after the addition of the Fe(II) solution at 15°C; at higher temperatures the reaction is faster. For reactions occurring at 36°C, voltammetry indicated that all apparent U(VI) was reduced by the Fe(II).

With reaction temperatures decreasing from 30°C, increasing negative biases are observed;[3] this indicates that the uranium is not quantitatively reduced in 30 seconds. Calculation of approximate heat of reaction shows the reduction reaction is endothermic; therefore, a reduction in the solution temperature favors the presence of the reactants, U(VI) and Fe(II), when equilibrium is established. This hypothesis was confirmed voltammetrically by recording a scan for an equilibrated solution at 15°C and again for the solution after it had been heated to 50°C and rapidly cooled back to 15°C to "freeze" the higher temperatures equilibrium. After reestablishment of the solution temperature at 15°C, the voltammetric scan indicated an increase in the U(IV) concentration and a decrease in the Fe(II) concentration.

Anodic voltammetric peaks for the oxidation of U(IV) and Mo(V) at a glassy carbon electrode occur within 0.02 V of each other. Due to the overlapping of the two peaks, changes affecting the two species cannot be differentiated and measured. Solution potentials and voltammetric scans during the oxidation reaction were recorded in the presence and absence of uranium in the reaction sequence. At 15 and 50°C, the presence of uranium produced a greater change in potential with time, following the color change of the reaction, than was observed without uranium present. The more rapid increase in potentials in the presence of uranium indicates the removal of an oxidizable species during the reaction. As the oxidation potentials of Mo(V) and U(IV) are nearly equal in the reaction matrix, the oxidation of U(IV) by HNO_3 must be considered.

The graphs of the potential changes during the oxidation reaction indicate that the reaction probably occurs in four stages: (1) the oxidation of Fe(II) by Mo(VI); (2) the oxidation of Mo(V) by HNO_3 with Fe(II) complexation of the NO produced; (3) the destruction of the $[Fe(NO)]^{+2}$ complex producing the color change and rapid release of gas; and, (4) an undetermined reaction producing a continuously increasing potential with time.

When Mo(VI), as an ammonium molybdate solution, is added to the reduction solution, changes of potential show that Fe(II) is immediately oxidized and an equilibrium is established. Due to the large complex ions formed by Mo(VI) with itself, H_3PO_4, Mo(V), and Fe(III), Mo(VI) is not quantitatively reduced by Fe(II) and may not be qualititatively oxidized by the HNO_3. The size of the complex ions is dependent upon acid concentrations. In the oxidation reaction solution, voltammetry indicates the continued presence of Fe(II) after apparent equilibrium conditions have been established. Below the normal oxidation reaction temperature (38°C), both Fe(II) and Mo(V) are apparent after equilibrium has been established. Decreasing the temperature produced increased equilibrium concentrations of the two species. From 38 to 50°C, Mo(V) is apparently quantitatively oxidized rapidly but Fe(II) is still apparent.

During the reaction, nitrogen oxide species are formed as detected by voltammetric peaks. In the presence of sulfamic acid, nitrites were not detectable and apparent concentrations of other nitrogen oxides were decreased. With increasing oxidation reaction solution temperatures, the presence of nitrogen oxides was increased. With continuous bubbling of N_2 through the solutions, the apparent concentration of the nitrogen oxides decreased with time.

Additional work is required to further confirm these observed effects and draw conclusions.

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1. L. Z. Bodnar and M. W. Lerner, NBL-272 (1974), p. 13.
2. B. W. Moran, NBL-297 (1981), p. 5.
3. A. C. Zook, L. H. Collins, and B. W. Moran, NBL-293 (1980), p. 1.
4. G. G. Rao and S. R. Sagi, Talanta 9, (1962), p. 715.

1.4 Nondestructive Determination of Uranium Enrichment Using Low Energy X and Gamma Rays (R. Hagenauer) A method has been developed to nondestructively determine uranium enrichments accurately using ^{238}U daughter gamma rays and thorium X rays produced from ^{235}U decay. The ^{238}U daughter gamma rays used in this method are ^{234}U gamma rays at 92.38 and 92.80 keV. The thorium X rays are produced from conversion electrons from ^{235}U decay. The energies for the $K_{\alpha 2}$ and $K_{\alpha 1}$ thorium X rays are 89.96 and 93.35 keV, respectively. Since sample self absorption from the ^{238}U doublet and thorium X rays will be nearly the same, the ratio of the 92-keV doublet and 89.96-keV X ray can be related to enrichment. Previous work by Dragnev[1] which showed promising results for low-enrichment samples has been developed further and extended to higher enrichments.

This technique has excellent application possibilities for safeguards inspectors. All data used in this report were taken with a hand-held Ge detector. An example of a typical low-energy spectrum is shown in Figure 1. By combining data from this low energy portion of the spectrum with data obtained from the 185.7-keV gamma-ray region, a single spectrum can be used to measure both ^{235}U content and enrichment. Since the gamma rays used in the peak area ratios are so close in energy, this method should also work with "infinitely thick" samples even if the matrix is unknown.

The success of the method is dependent on resolving the 93.35-keV X ray from the 92-keV doublet of ^{238}U. Two techniques have been employed to separate this X ray from the adjacent gamma rays. The first technique utilized the "STRIP" function on multichannel analyzers. The second technique used peak-fitting routines to determine the correct peak areas.

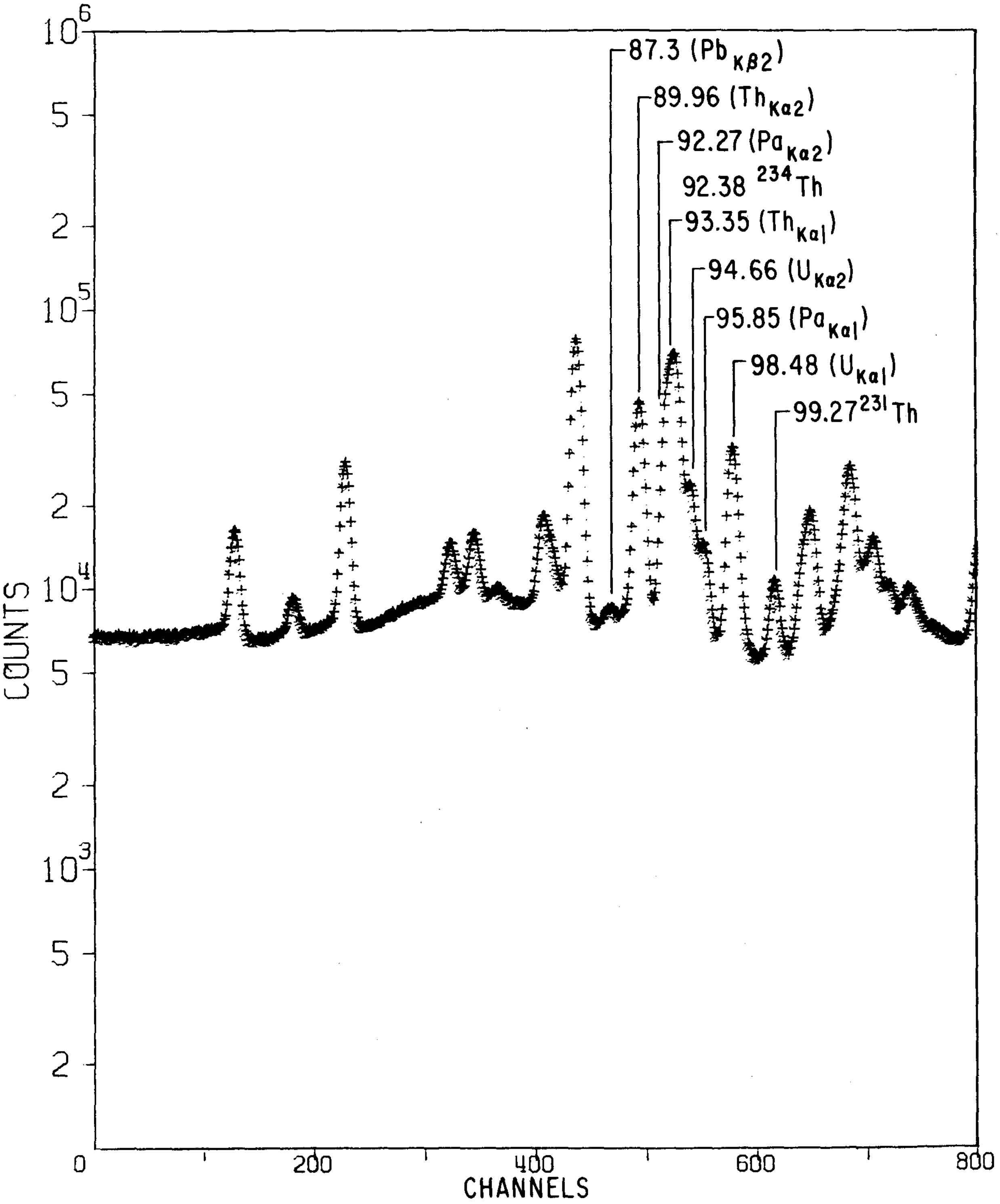

Figure 1

Gamma and X-Ray Spectrum of Enriched Uranium

Good estimates can be obtained simply by using a "STRIP" function available on most new multichannel analyzers. First store an "enriched" spectrum of uranium enriched to 99.9% in ^{235}U in a separate portion of the analyzer memory. Then normalize the "enriched" spectrum to the 89.96-keV X-ray peak of the sample spectrum and subtract the normalized "enriched" spectrum from the sample spectrum. The resultant stripped spectrum contains the cleanly resolved ^{238}U gamma-ray doublet at 92 keV. The 92-keV peak area from the stripped spectrum and the 89.96-keV X-ray peak area from the original sample spectrum are used to obtain the $^{238}U/^{235}U$ ratio. This simplified technique works well for enrichments up to 20%. At higher enrichments, however, slight gain shifts or peak broadening differences between sample and reference ^{235}U spectra can cause large errors in the 92-keV peak.

A peak-fitting routine GRPANL[2] has been used by Gunnink to determine plutonium 238, 239, 240, and 241 isotopes.[3] The same program was used in the present work to resolve the uranium spectrum and separate the ^{238}U activity from the lead, uranium, protactinium, and thorium X rays.

Spectra were taken with a Ge detector with an efficiency of 11% and a resolution (FWHM) of 0.80 keV at 100 keV. The energy region from 87 to 100 keV includes X-rays from lead shielding, thorium, and protactinium X rays from ^{235}U decay, and uranium X rays from alpha-induced fluorescence as well as the ^{238}U gamma rays. A list of the energies of the X and gamma rays is given in Table I.

TABLE I

Gamma and X Rays Used in the GRPANL Peak Fit

Gamma Ray Energy	Isotope
87.3	$Pb_{K\beta2}$
89.96	$Th_{K\alpha2}$
92.27	$Pa_{K\alpha2}$
92.32	^{234}Th
92.79	^{234}Th
93.35	$Th_{K\alpha1}$
94.66	$U_{K\alpha1}$
98.48	$U_{K\alpha1}$
99.27	^{231}Th

Standards were prepared from existing uranium foils of various enrichments and by mixing U_3O_8 of known uranium enrichment with a light matrix material, Li_2CO_3, to minimize self absorption. Counting times for samples varied with uranium content. Typically, a small sample containing 500 mg of uranium required 4000 sec to acquire enough counts for a good computer fit. The relationship between the peak area ratios and enrichment is shown in Figure 2 and Table II.

TABLE II

Results of Enrichment Determination

Peak Area Ratio, U-238/U-235	Enrichment, Wt% ^{235}U Accepted Value	Enrichment, Wt% ^{235}U Experimental Value	Difference
55.7	00.27	00.33	+0.06
22.2	00.71	00.83	+0.12
11.4	01.64	01.60	+0.04
4.34	04.13	04.12	-0.01
1.56	10.10	10.66	+0.56
0.93	15.78	16.69	+0.92
0.75	19.90	19.84	-0.06
0.68	21.00	21.31	+0.31
0.48	28.33	27.86	-0.47
0.28	40.00	39.87	-0.13
0.12	60.00	59.82	-0.18

A relationship between enrichment, E, and the 92/89.96-keV peak area ratios, R, can be obtained as follows:

$$E = \frac{100 \times \text{w.f.U-235}}{\text{w.f.U-234} + \text{w.f.U-235} + \text{w.f.U-236} + \text{w.f.U-238}}$$

where: w.f.U-234, U-235, U-236, U-238 = weight fraction U-234, U-235, U-236, U-238, respectively.

For a close approximation we can assume that:

$$\text{w.f.U-234} + \text{w.f.U-236} = 0.01\ \text{w.f.U-235}$$

thus: $$E = \frac{100}{1.01 + \frac{\text{w.f.U-238}}{\text{w.f.U-235}}} = \frac{100}{1.01 + kR}$$

where k is an experimental constant that is a function of detector efficiency, half-lives, atomic weights and gamma-ray branching ratios.

The constant, k, was determined in an iterative manner to give the best fit to the calibration data. For our detector system, k was found to be 5.45. This is close to the theoretical value derived in Appendix A.

The average absolute difference between the accepted enrichment value and the measured value as seen in Table II is only 0.25% over the enrichment range of 0.3% to 60%. At higher enrichments the 93.35-keV X ray masks the much weaker ^{238}U activity and the errors increase rapidly as enrichment increases. At these enrichments high-resolution Low-Energy Photon Spectrometer (LEPS) Ge detectors should resolve the peaks and attempts will be made to extend the range of the method with such a detector.

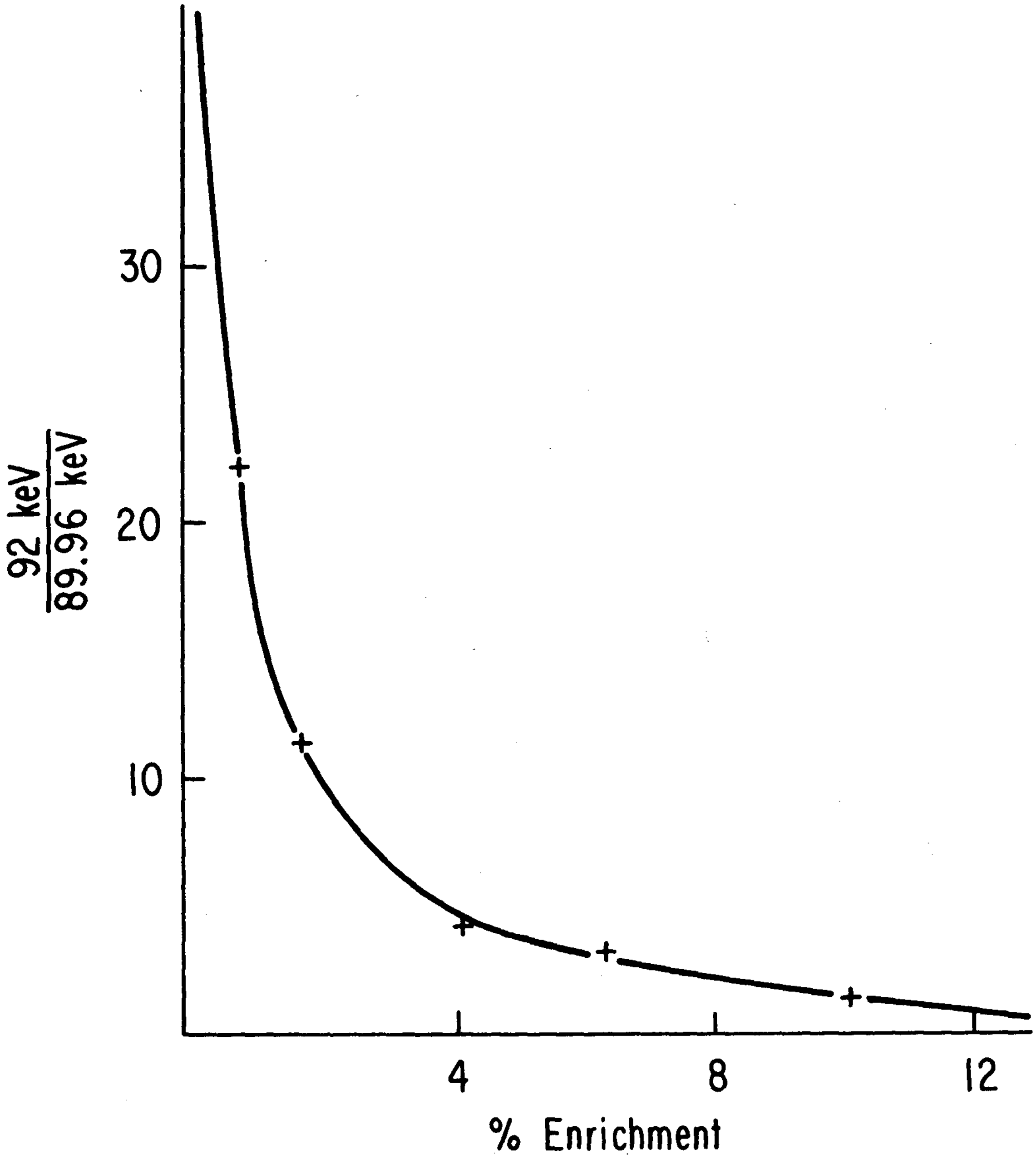

Figure 2

Relationship Between Peak Area Ratios
and Enrichment

Appendix A

Theoretical Calculations of Experimental Constants Used for Enrichment Calculations

$$E = \frac{100}{1.01 + \frac{\text{w.f.U-238}}{\text{w.f.U-235}}} = \frac{100}{1.01 + \frac{238 \times N_{238}}{235 \times N_{235}}}$$

$$A = N\lambda$$

$$N_{238} = \frac{PA_{238}}{\lambda \times \varepsilon_{238} \times BR_{238}} = \frac{PA_{238}\ T_{238}}{\varepsilon_{238} \times BR_{238} \times 0.693}$$

$$E = \frac{100}{1.01 + \frac{PA_{238} \times T_{238} \times \varepsilon_{235} \times BR_{235} \times 238}{PA_{235} \times T_{235} \times \varepsilon_{238} \times BR_{238} \times 235}} = \frac{100}{1.01 + k\ R}$$

$$\text{where } k = \frac{1.647 \times 10^{12} \text{ days} \times 0.33 \times 10^{-2} \times 2.45 \times 10^{-2} \times 238}{2.604 \times 10^{11} \text{ days} \times 0.38 \times 10^{-2} \times 2.50 \times 10^{-2} \times 235} = 5.45$$

where: N = number of atoms of the corresponding isotope

PA = peak area of the corresponding isotope

ε = detector efficiency of the gamma ray

BR = branching ratio of the corresponding isotope

T = half-life of the corresponding isotope

A = activity of the isotope

λ = decay constant

This result agrees with the value of k experimentally determined within the error limits of the branching ratios and detector efficiency.

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1. T. N. Dragnev and B. P. Damjanov, IAEA-SM-231/130, (1978) pp. 739-752.

2. R. Gunnink, UCRL-52917 (1980).

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2. PLUTONIUM

2.1 <u>An Interlaboratory Evaluation of a Proposed Standard Method for the Controlled-Potential Coulometric Determination of Plutonium</u> (C. D. Bingham and M. K. Holland) An interlaboratory comparison was designed to evaluate a method proposed for consideration by the American Society for Testing and Materials (ASTM). The method is for the determination of plutonium concentration in plutonium dioxide using controlled-potential coulometry.

The proposed method allows the user a choice of electrolyte solutions and of materials used for constructing the generator electrode. It also permits a choice of instrumentation using either analog or digital integration with calibration by either chemical or electrical means.

Measurements on two separate samples of plutonium dioxide sampled from the same master batch were performed by five laboratories: Allied-General Nuclear Services, Barnwell, SC (AGNS); Los Alamos National Laboratory, Los Alamos, NM (LA); Mound Laboratory, Miamisburg, OH (ML); the Department of Energy New Brunswick Laboratory, Argonne, IL (NBL); and the DuPont Savannah River Plant, Aiken, SC (SRP). These laboratories had varied experience with coulometry in general and with the proposed method in particular. Each laboratory was requested to subdivide each sample, to fire each subsample in air to constant weight at 950°C, to dissolve each subsample, and to assay one aliquant of the solution on each of two separate days. Thus, four measurements on each sample were made by each participant (see Figure 1). One laboratory, in order to enlarge the statistical base of data, volunteered to perform independent measurements as two separate laboratories.

The sample vials each containing approximately 2 g of PuO_2 were prepared and distributed by NBL. Data were reported to and statistically evaluated by NBL. The sample material had been characterized by NBL with the assigned plutonium concentration determined by assay based upon preignition of the material at 950°C. The atomic weight used in the assay calculation was determined by thermal ionization mass spectrometry and the value provided to all participating laboratories.

Data reported by the participating laboratories and corrected as described below are tabulated in Table 1. Codes are used to maintain laboratory anonymity. Reported data were corrected by NBL for radioactive decay to a common date (12/1/80), for iron interference where such a correction was not performed by the participant, and for an atomic weight value not being that specified. Data are graphically displayed in Figures 2-4. Figure 2 shows the values reported for each subsample solution aliquant. Figure 3 shows the mean of the reported values for each subsample. Figure 4 shows the range between the reported values of each subsample solution aliquant.

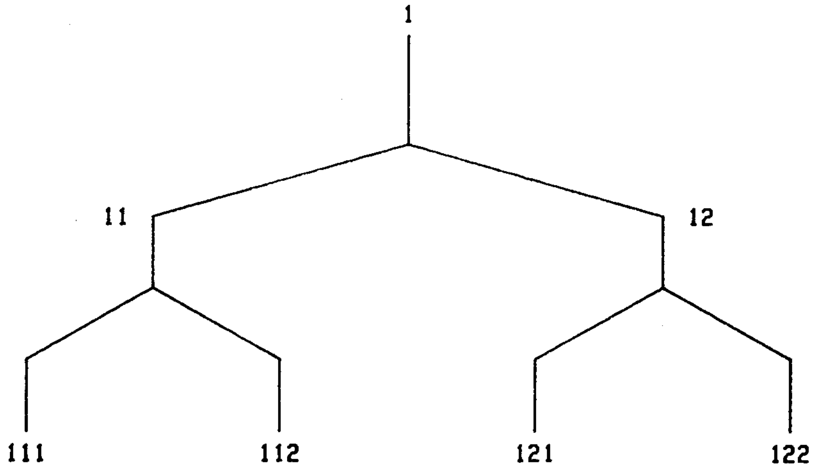


Figure 1
Example Sample Code

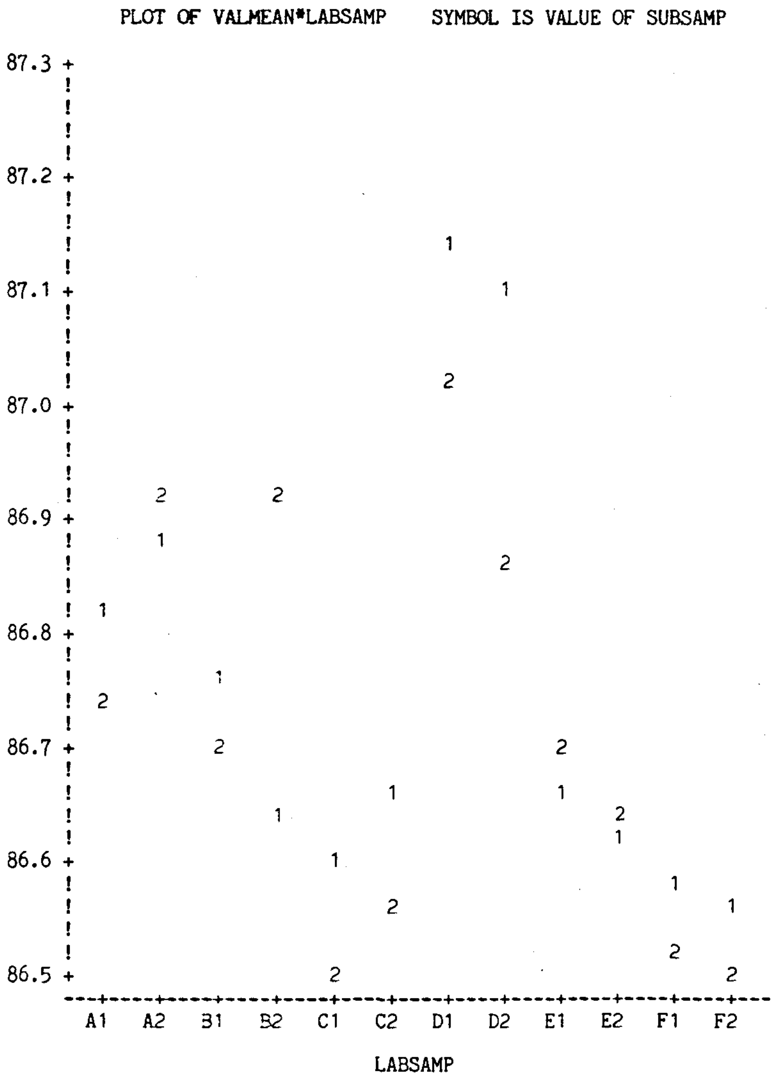


Figure 3
Interlaboratory Evaluation of Proposed ASTM Coulometry Method

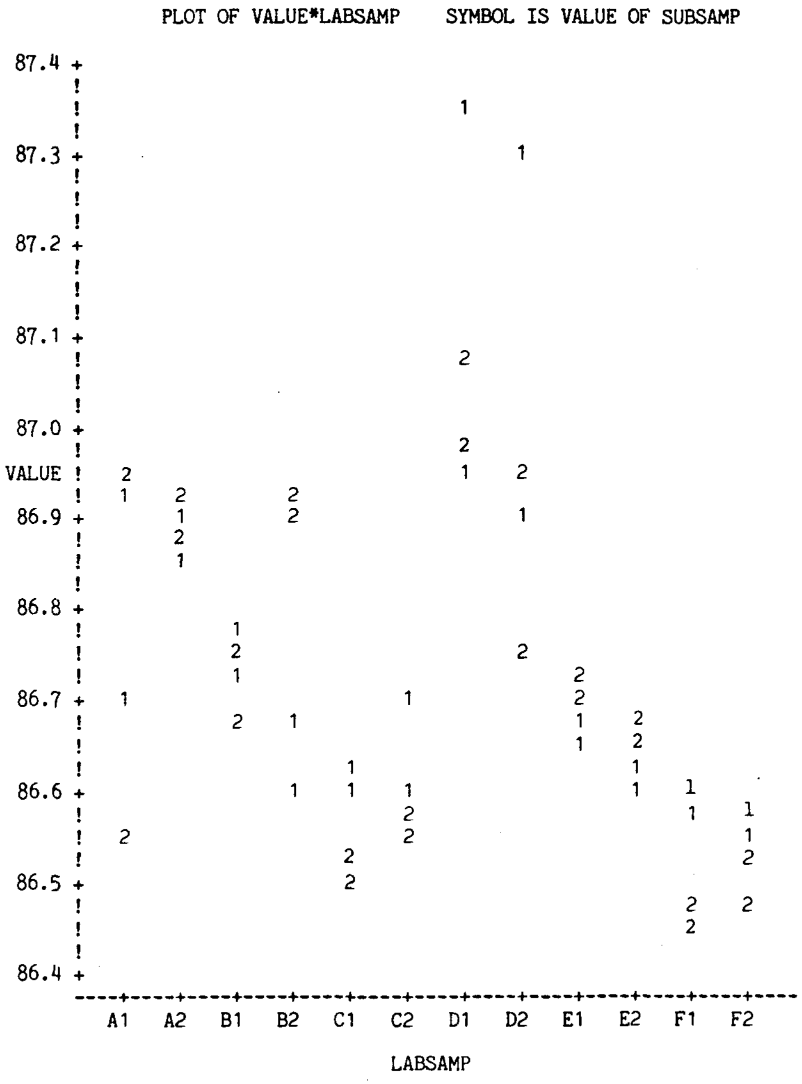


Figure 2
Interlaboratory Evaluation of Proposed ASTM Coulometry Method

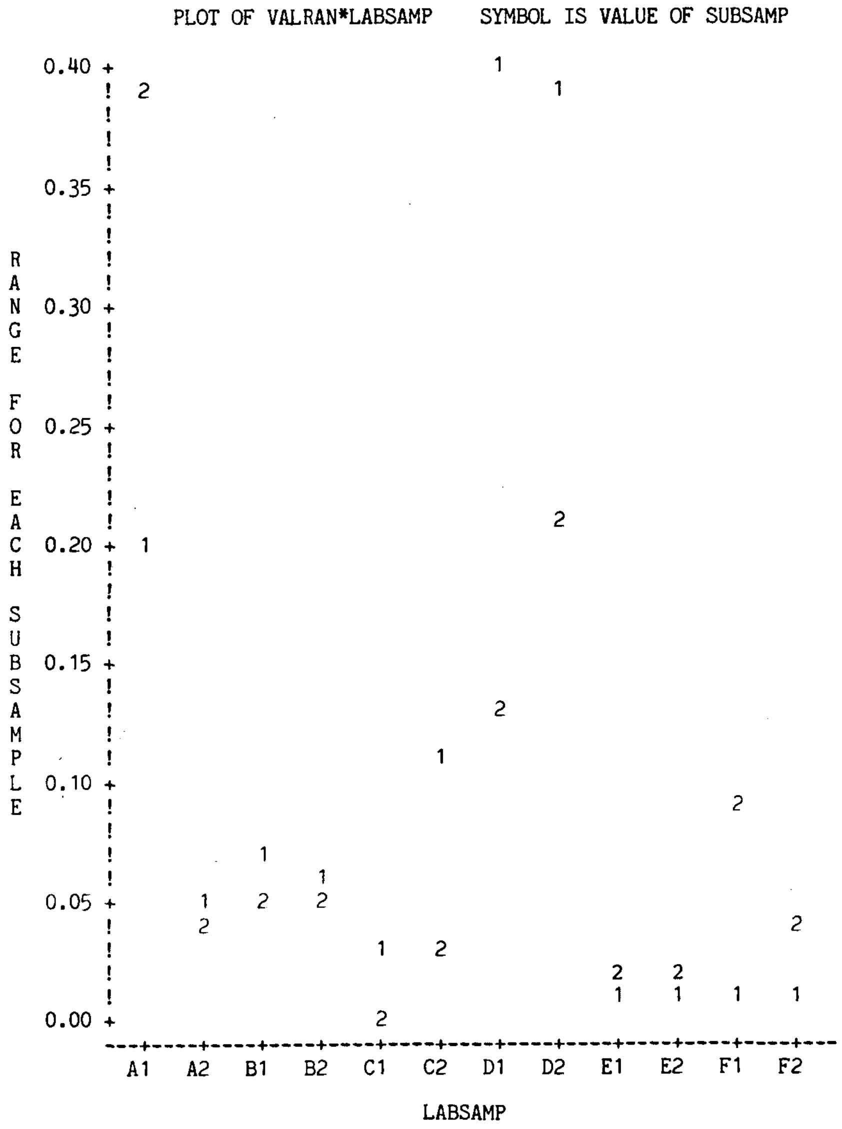


Figure 4
Interlaboratory Evaluation of Proposed ASTM Coulometry Method

TABLE I

Summary of Corrected Values, Wt.% Pu

LAB	111	112	121	122	211	212	221	222	$\bar{x}_\ell$, s_ℓ	$\frac{(\bar{x} - \mu)}{\mu}100$
A	86.915	86.712	86.934	86.548	86.912	86.860	86.889	86.933	86.8379 0.1377	0.1869
B	86.785	86.716	86.669	86.721	86.604	86.664	86.891	86.936	86.7483 0.1152	0.0835
C	86.620	86.592	86.505	86.510	86.712	86.606	86.576	86.547	86.5835 0.0670	-0.1067
D	86.952	87.347	86.950	86.083	87.903	87.290	86.745	86.955	87.0281 0.2023	0.4063
E	86.654	86.668	86.717	86.703	86.606	86.618	86.622	86.634	86.6528 0.0407	-0.0267
F	86.580	86.571	86.566	86.476	86.560	86.554	86.487	86.523	86.5396 0.0397	-0.1573

$\bar{\bar{x}}$ - 86.732 (N=48) 0.065
s - 0.200
$s_{\bar{\bar{x}}}$ - 0.029

$\bar{\bar{x}}$ - 86.672 (N=40) -0.004_5
s - 0.139
$s_{\bar{\bar{x}}}$ - 0.022

μ (12/1/80)
$86.675_9 \pm 0.052_3$ (95% C.L. on mean)

Statistical analysis of the data identified the results from Laboratory D as statistical outliers. The mean of the remaining values (N = 40) is 86.672 ± 0.022 wt% (uncertainty is standard deviation of the mean). The assigned value of the plutonium concentration for the plutonium dioxide is 86.676 ± 0.052 wt% (uncertainty represents 95% confidence limits). The interlaboratory mean differs from the assigned value by -0.004% relative difference - a difference which is not statistically significant.

A number of participants indicated that use of some commercially available instrumentation was not completely compatible with the directions written in the method. Whereas there was some validity to the claim, there did not appear to be a completely clear understanding of the application of the "potential adjustment technique" written into the method or of the fact that the use of the method required bipolar response of the integrator. Further, it was not understood that measurements of the "solution redox potentials" must be made while a controlled-potential is applied to the working electrode and when there is essentially no current flowing. Once the controlled potential has been removed, then the solution potential will rapidly return to a value defined by the redox equilibrium of the chemical system. Editorial changes to the proposed method were suggested which added clarifying instructions.

For laboratories which already had cell and stirrer designs which permitted short titration times (i.e., low "cell constants"), the claim in the method of "considerable reduction in operating time" was not substantiated. Another laboratory observed a 25% reduction over measurement time normally experienced but indicated that the proposed method required more careful attention to the operation than the method currently used.

Comments were received regarding the effect of temperature variations in the laboratory on the electrical calibration factor. Variations of 0.04%/^{o}C were reported for some instrumentation. The method (section 13.1) indicates that temperature stability of the laboratory is required in order to achieve optimum instrument performance; however, temperature control specifications for a laboratory were not a requirement of the method.

One of the tenets inherent in the use of a standard method is a fairly detailed familiarity with the method. Although the participating laboratories all used controlled-potential coulometry for the assay of plutonium-containing materials, not all were experienced in the application of the "potential adjustment technique" nor in the theory underlying its application. This inexperience gave rise to non-standard implementation of the method.

Quality of laboratory equipment and quality of the laboratory environment in which the equipment is required to operate have a strong influence on the quality of measurement results. Section 13 of the proposed method addresses quality for instrumental components necessary to achieve optimum performance.

The values calculated for repeatability and reproducibility intervals are larger than anticipated based upon data accumulated by one laboratory over an extended period of time. Although it was not required by the test protocol (and maybe should have been), some laboratories ran and reported the results on standards measured on the same days using the proposed method. If these reported values would have been used to apply corrections for systemmatic errors, the range for the reported sample values would have been markedly reduced, thereby reducing the between-laboratory component of variance.

Choice of electrolyte was left to the participating laboratory. Four laboratories used 0.5$\underline{M}$ H_2SO_4 and two laboratories used 0.9$\underline{M}$ HNO_3. Similarly, a choice of working electode material was left to the laboratory. Four laboratories used a platinum working electrode and two laboratories used a gold working electrode. The reported measurement data provide no evidence that differences in electolyte or electrode material contribute to systematic errors.

The interlaboratory mean (excluding results from Laboratory D) shows excellent agreement (-0.004% relative difference) with the value assigned by independent characterization measurements. The advantage of electrical calibration of the instrumentation which provides an independent path for traceability cannot be overemphasized. Independent verification of performance quality can thus be demonstrated in the laboratory by measuring appropriate reference materials and using control chart methods.

2.2 Evaluation of a Commercially Available Digital Coulometer (M. K. Holland and K. Lewis) An MT Model 3 Controlled-Potential Coulometer has been used in the development of the New Brunswick Laboratory Controlled-Potential Coulometric Method for the Determination of Plutonium.[1] Although techniques had to be developed to correct for errors due to analog integration in the MT instrument, results using the corrections were very satisfactory. Further work at NBL led to the development of the NBL Model FH-1 digital integrator[2] for use with the potentiostat module of the MT instrument. The digital integrator has proven to be highly reliable and has essentially eliminated previous integration errors. The MT coulometer is no longer commercially available, so alternative sources of coulometric instrumentation were sought. EG&G Princeton Applied Research (PAR), which markets a variety of electrochemical instruments, has two modules - a potentiostat/galvanostat model 173 and a digital coulometer model 179 - with specifications which were worth investigating at NBL. These instruments were purchased and, as part of a total evaluation of their capabilities, their use for the controlled-potential coulometric determination of plutonium was examined and is reported here. The EG&G PAR equipment was evaluated for its applicability in the NBL method for plutonium assay by performing constant current electrical calibrations and controlled-potential coulometric determinations of plutonium. The operating parameters of the NBL method dictated the selection of the instrument settings given in Table I.

TABLE I

Instrument Settings

Potentiostat Operating Mode:	Constant E
Integrator Mode:	Bipolar
Integrator Scale:	100 mA
Integrator Compensator:	Off

A series of constant-current calibrations was performed using the equipment and procedure developed for electrical calibration at NBL.[3] The appropriate controlled-potential was applied to a 100 Ω precision resistor to achieve the desired constant current. On the 100-mA setting, required for plutonium determination, the EG&G PAR digital coulometer failed to integrate electrolysis currents less than 12μA. Integrator non-linearity increased rapidly as the 12-μA lower limit was approached. Table II shows comparisons of calibration data for the EG&G PAR instrument and the instruments now used for plutonium determinations at NBL. All three instruments have comparable precisions, although the MT Model 3 analog instrument is the most precise. The linearity, shown as the change in the calibration value with the current range used, is considerably poorer for the EG&G PAR unit compared to the two instruments used at NBL. The effect of the observed non-linearity of the EG&G PAR instrument upon the measurement of a 10-mg plutonium aliquot using the NBL method for plutonium determination was estimated to be < ± 0.05%. The integrator display readability further increases the uncertainty by 0.01%.

TABLE II

Precision and Linearity of Constant Current Calibrations

	EG&G PAR		MT Model 3 (Analog)		NBL AUTOCOULOMETER (Digital)	
Current, mA	RSD,%	% Diff. from 50-mA Value	RSD,%	% Diff. from 50-mA Value	RSD,%	% Diff. from 50-mA Value
50	0.003		0.002		0.002	
25	0.001	+0.020	0.002	+0.001	0.002	0.000
10	0.003	+0.024	0.002	+0.002	0.002	0.000
1	0.009	+0.198	0.002	+0.016	0.010	+0.005
0.1	0.136	+2.719	0.019	+0.206	0.130	+0.025
0.05	0.330	+7.154	0.030	+0.373	0.129	+0.308
0.01	—	*	0.113	+2.102	0.447	+0.854

*Instrument did not integrate current <12 μA

A further evaluation of the EG&G PAR instrument was made by performing controlled-potential coulometric determinations on weighed portions of a plutonium solution. Results are shown in Table III for both the EG&G PAR coulometer and the MT Model 3 coulometer system used at NBL. The NBL method for controlled-potential coulometry was used for all determinations.

TABLE III

Coulometric Determination of Plutonium

Instrument	Recovery, %	n	RSD, %
EG&G PAR	100.13	4	0.05
MT Model 3	100.01	7	0.03

The systematic error, greater than 0.1%, exhibited by the EG&G PAR coulometer is outside the acceptable limits for plutonium determinations at NBL and would require the use of chemical calibration to utilize this instrument. Additional evaluation work on the EG&G PAR coulometer is planned to determine whether the instrument can be adapted for use at NBL.

REFERENCES

1. M. K. Holland, J. R. Weiss, and C. E. Pietri, NBL-299 (1981), p. 6.

2. T. L. Frazzini, M. K. Holland, J. R. Weiss, and C. E. Pietri, NBL-293, (1980), p. 27.

3. M. K. Holland, J. R. Weiss, and C. E. Pietri, NBL-299 (1981), App. D.

2.3 A Comparison of Controlled-Potential Coulometric End Point and Calibration Procedures Using the NBL AUTOCOULOMETER (M. K. Holland, K. Lewis, J. R. Weiss, and C. E. Pietri) The New Brunswick Laboratory automated coulometer (AUTOCOULOMETER) designed for the controlled-potential coulometric determination of plutonium has been previously described.[1] This instrument utilizes electrical calibration and the control potential adjustment technique to determine the end point of the electrolysis. Controlled-potential coulometry of plutonium has been performed by others using chemical calibrations and a number of alternative end point procedures including electrolysis to a fixed current cut-off, electrolysis to a fixed time cut-off and the predictive end point technique.[2] Since the AUTOCOULOMETER has the software capability to utilize any of the end-point techniques noted, it was recognized that a comparison of the results obtained by the different methods could be made concurrently during a determination. Results of such a comparison of selected techniques made on a number of determinations are reported here.

Three end point techniques (75-μA current cut-off, 300-sec time cut-off and the predictive end point) were evaluated by comparing the results obtained by these methods to that obtained using the NBL method as a reference value. All of the chosen techniques utilized conditions attained during the use of the NBL method, and thus a direct comparison of the techniques could be made concurrently during a determination eliminating the effects of sample preparation errors. The AUTOCOULOMETER was programmed to obtain the data for all the techniques during each run; results from 147 runs are given in Table I.

TABLE I

Comparison of Selected End Point Procedures
Using Electrical Calibration

End-Point Procedure	Mean Recovery, %*	n	RSD, %
Predictive	100.01	147	0.01
300-sec Time Cut-off	99.79	147	0.17
75-μA Current Cut-off	99.90	147	0.05

* Based on NBL method as reference value

The predictive end-point technique agrees extremely well with the NBL method; this would be expected since both techniques are based on the fundamental principles of coulometry. The arbitrary cut-off end points give lower recoveries and the values obtained would vary with the cut-off points chosen; the current cut-off results are relatively precise but the time cut-off results would be unacceptable at the level shown.

The two arbitrary cut-off procedures could be chemically calibrated to eliminate the biases obtained. This is illustrated by the data in Table II. Forty-one of the 147 runs were quality assurance standards; these 41 values were used to calculate a chemical correction factor which was applied to the remaining 106 determinations with the results shown in the Table II.

TABLE II

Effect of Chemical Calibration on Selected End Point Procedures

End-Point Procedures	Mean Recovery, %*	n	RSD, %
300-sec Time Cut-off	99.98	106	0.21
75-μA Current Cut-off	99.99	106	0.04

*Based on chemical calibration factor obtained from 41 standards

It is apparent that chemical calibration can be usefully applied when the chosen end point is reasonably precise such as the 75-μA current cut-off in Table II. It is desirable to utilize techniques based on the fundamental principles of coulometry such as the NBL method or the predictive method, especially when instrumentation such as the AUTOCOULOMETER is available since the implementation of these methods then requires no additional effort.

REFERENCES

1. M. K. Holland, J. R. Weiss, and C. E. Pietri, NBL-299 (1981).

2. F. B. Stephens, F. Jakob, L. P. Rigdon, and J. E. Harrar, Anal. Chem. 42, 764 (1970).

2.4 Evaluation of an Ion-Exchange Method for the Separation of Trace Amounts of Uranium from Plutonium (C. G. Cacic, A. C. Zook, G. A. Sowell, J. R. Weiss, and C. E. Pietri) An ion-exchange method capable of separating trace amounts of uranium from plutonium has been developed at the Los Alamos National Laboratory[1] and is being evaluated for use at the New Brunswick Laboratory. Los Alamos data show a recovery of 97.5% uranium and a high separation factor of $>10^6$ for plutonium. Application of this method to the determination of uranium as an impurity or as in-growth from plutonium decay is important in the characterizeration of reference materials for safeguards purposes.

The procedure involves dissolution of the plutonium in 9M HBr followed by oxidation of uranium to U(VI) with bromine and sorption of uranium (and plutonium, in part) on Dow MSA-1 chloride-form anion resin. Any higher oxidation states of plutonium are reduced to Pu(III) and eluted from the column with 0.1M HI-12M HCl, and the purified uranium is eluted with 0.1M HCl. The separated uranium is then assayed using pulsed-laser fluorometry.[2]

Initial work included evaluation of the uranium content of reagents, which was found to be satisfactory for this study, Table I. Since HCl, HBr, and HI, and the liquid bromine used in the procedure are extremely corrosive to stainless steel glove boxes, the following precautions were used to keep corrosion at a minimum: (1) the ion-exchange operation was done in a separate, physically-isolated glove box; (2) the amount of corrosive reagents in the box was kept to a minimum; (3) the waste was processed immediately; and, (4) the glove box was washed down after each ion-exchange separation was completed.

The method was applied to the separation of uranium in several plutonium samples from the Plutonium Metals Exchange Program. NBL results are in agreement with those reported by other participating laboratories,[3] Table II.

These initial results show promise for the development of this procedure for the routine separation of trace uranium in plutonium prior to determination. Further studies are planned to determine the uranium recovery and the plutonium separation factor using uranium-plutonium reference materials, and to monitor the effects of iron and americium on the system.

TABLE I

Determination of Uranium in Reagents(a)

		Uranium Content	
Reagent(b)	Volume Sampled, mL	Total U, ng	ng U/mL
H_2O, millipore	20	<10	<0.5
HCl, conc.	20	<20	<1
HNO_3, conc.	20	100	5
HBr, conc.	20	<20	<1
HI, conc.	10	30	3
Br, liquid	10	<10	<1

(a) U measured by pulsed-laser fluorometry

(b) Reagent grade chemicals

TABLE II

Determination of Uranium in Plutonium Metals Exchange Samples

	X Metal		Y Metal	
	U Found, µg/g[a]	SD	U Found, µg/g[a]	SD
NBL average[b]	55.6	1.5	51.2	2.4
Exchange average[c]	56.8	16.4	53.8	14.1

(a) Based on initial uranium impurity content and in-growth from Pu-239 decay.

(b) Average of three determinations corrected to June, 1980.

(c) Average from duplicate determinations by five participating laboratories corrected to June, 1980.

REFERENCES

1. S. F. Marsh, LA-8399, August, 1980.

2. A. C. Zook, L. H. Collins, and C. E. Pietri, Mikrochim. Acta (Wien), 1981 II, 457 (1981).

3. Rockwell Hanford Operations, "Americium, Neptunium, and Uranium Data", presented at the Plutonium Metals Exchange Meeting, McClellen Air Force Base, California, November 14-15, 1980.

B. ISOTOPIC COMPOSITION

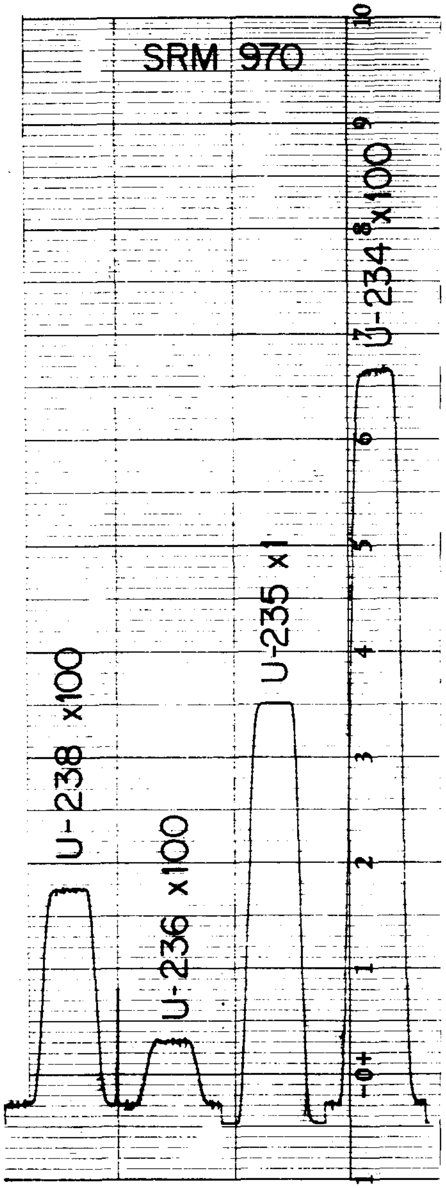
1. A Totally Programmable Magnet Field Control System for a 30-cm Radius, 90-Degree Magnet Sector Mass Spectrometer (V. E. Connolly and F. P. Orlowicz) Satisfactory measurement of the isotopic abundance of uranium materials using thermal ionization mass spectrometers equipped with current-controlled magnet systems requires extensive conditioning of the magnet at the operational range and a carefully planned switching sequence which must be rigorously followed in order to minimize problems due to magnet hysteresis. In addition, existing magnet power supplies in use at the laboratory which utilize electron-tube design have required increasingly more frequent and expensive repairs. In

order to improve the reliability and operation of the mass spectrometers, a solid-state field control system was considered which would allow random switching over a wide range to any field strength required.

A low-voltage, solid-state field control system including new magnet coils was purchased from Nuclide Associates, Inc. and installed on a 30-cm radius, 90-degree magnet sector mass spectrometer equipped with a Hewlett-Packard 9825A programmable calculator based data acquisition system.[1] Control of the magnet is achieved through two 0 to ±10 V digital to analog (D/A) cards in the multiprogrammer. The resolution of each card is 5 mV and the signals are fed into a summation amplifier card with the signal from one of the cards being reduced by a factor of 20 to yield a fine resolution of 0.25 mV for that card. Thus, the control signal for the system ranges from 0 to ±10.5 V in 5- and 0.25-mV steps. The resulting signal is then fed into the drive circuit of the Hall Probe. Voltages on the Hall Probe for the uranium and rhenium spectra are approximately 5.7 and 5.1 V, respectively, using an accelerating voltage of 12 kV.

The complete program for the instrument was rewritten for the field control system and incorporates several new subroutines. The first is a "Test Scan" subroutine that steps over each isotope range by unit increments of the fine D/A card, takes a short reading (1/10 of the normal reading cycle) at each position, and prints the card input value and the resulting reading. There are approximately 50 steps peak-to-peak per mass unit in the uranium range and, from the resulting printout, the best values for peak center and baseline values can be determined. A typical scan and printout for National Bureau of Standards (NBS) SRM 970 is shown in Figure 1 and demonstrates sharp, well defined, flat-topped peaks with little or no tailing from the large (97.6%) U-235 peak to the U-234 and U-236 peaks. Close examination of numerous scans showed a tendency for a slight rounding of the peaks on the high mass side. However, the range across the flat part of the peak (> 1/3 peak width) is more than sufficient for acceptable measurement capabilities. On the basis of these scans, it was determined that approximately 50% peak height was ± 13 steps from the peak center value as demonstrated in Figure 1 for the range from the 0.15% U-236 isotope to the 97.6% U-235 isotope. This information was incorporated in a second subroutine to automatically test for the U-235 and U-238 peak centers during the final stabilization period of the sample analysis procedure. The test used nominal peak center values to read the baseline, peak center height, and readings plus and minus 13 steps from the peak center value for each of the major isotopes. The mid-peak values must be >25%<75% of the full peak height to pass the test. The test is very stringent since the peak center values must be within ± 1 step of the true peak center. In Figure 1, the peak center values would pass at ± 1 step for the U-234, U-235, and U-236 peaks, but fail for the U-238 peak since the true input value for this peak is halfway between 1344 and 1345. If 1346 was used, the test at the low mass side midpoint would fail. When the test fails, the calculator prints all the readings used for the test so the analyst can determine the direction and magnitude of any shift in the spectrum. The analyst now has the option to shift all the nominal values via a semi-automatic keyboard function and repeat the test or execute the "Test Scan". After the peak center test is passed, another measurement is made for any possible U-233 in the sample and a U-233/U-235 ratio is printed. If, on the basis of this value, there appears to be U-233 in the sample, a measurement can be made during the analysis of the sample.

An evaluation of the instrument using a three-point calibration with NBS SRM U-100, U-500, and U-900, as well as the analysis of a sample containing ~0.05% U-233, demonstrated good performance of both the field control system and the program. Table I lists individual control runs on NBS SRM U-030 and summarizes data for several additional SRM's. (For computational purposes, a fourth decimal place for the U-235 and U-238 NBS values has been added and is based on NBL best estimates.[2] The table also includes results for a routine inventory verification sample containing U-233, but of a poorer quality than usual, i.e., low uranium content with some impurities. Review of the data shows that one lower result on the U-234 isotope (0.0106%) on SRM U-020 contributed to a high relative standard deviation (RSD) and a low average. In addition, on the first two SRM U-970 runs there was a problem with too short a wait time before reading the peaks. Overall, the results show good precision and accuracy using a relatively reliable and trouble-free system.



```
                          STEP SCAN  SRM 970

       U-234                U-235                U-236                U-238
  INPUT  READING       INPUT  READING       INPUT  READING       INPUT  READING
==============================================================================
I= 1120  0.1311      I= 1170  0.0019      I= 1220  0.1727      I= 1320  0.1724
I= 1121  0.2084      I= 1171  0.0019      I= 1221  0.1874      I= 1321  0.1681
I= 1122  0.1969      I= 1172  0.0019      I= 1222  0.1741      I= 1322  0.1876
I= 1123  0.2015      I= 1173  0.0019      I= 1223  0.1945      I= 1323  0.1717
I= 1124  0.1856      I= 1174  0.0030      I= 1224  0.1897      I= 1324  0.1738
I= 1125  0.2013      I= 1175  0.0101      I= 1225  0.1898      I= 1325  0.1866
I= 1126  0.2409      I= 1176  0.0280      I= 1226  0.1828      I= 1326  0.1966
I= 1127  0.3176      I= 1177  0.0716      I= 1227  0.1914      I= 1327  0.2712
I= 1128  0.5102      I= 1178  0.2001      I= 1228  0.2125      I= 1328  0.3555
I= 1129  0.9249      I= 1179  0.4587      I= 1229  0.2586      I= 1329  0.5579
I= 1130  1.6377      I= 1180  0.8650      I= 1230  0.3350      I= 1330  0.8414
I= 1131  2.5729      I= 1181  1.3732      I= 1231  0.4176      I= 1331  1.1290
I= 1132  3.6893      I= 1182  2.0159      I= 1232  0.5221      I= 1332  1.4402
I= 1133  4.6917      I= 1183  2.6214      I= 1233  0.5920      I= 1333  1.7261
I= 1134  5.5953      I= 1184  3.1781      I= 1234  0.6593      I= 1334  1.9565
I= 1135  6.2704      I= 1185  3.5134      I= 1235  0.7240      I= 1335  2.0790
I= 1136  6.6897      I= 1186  3.7426      I= 1236  0.7303      I= 1336  2.1130
I= 1137  6.7936      I= 1187  3.8026      I= 1237  0.7419      I= 1337  2.1212
I= 1138  6.8021      I= 1188  3.8098      I= 1238  0.7182      I= 1338  2.1229
I= 1139  6.8035      I= 1189  3.8103      I= 1239  0.7610      I= 1339  2.1239
I= 1140  6.7947      I= 1190  3.8104      I= 1240  0.7440      I= 1340  2.1225
I= 1141  6.8103      I= 1191  3.8090      I= 1241  0.7356      I= 1341  2.1194
I= 1142  6.7832      I= 1192  3.8085      I= 1242  0.7486      I= 1342  2.1150
I= 1143  6.8000      I= 1193  3.8079      I= 1243  0.7426      I= 1343  2.1264
I= 1144  6.8003      I= 1194  3.8067      I= 1244  0.7420      I= 1344  2.1213
I= 1145  6.7719      I= 1195  3.8061      I= 1245  0.7493      I= 1345  2.1271
I= 1146  6.7887      I= 1196  3.8044      I= 1246  0.7445      I= 1346  2.1128
I= 1147  6.7954      I= 1197  3.8028      I= 1247  0.7450      I= 1347  2.1408
I= 1148  6.8050      I= 1198  3.8014      I= 1248  0.7357      I= 1348  2.1171
I= 1149  6.7752      I= 1199  3.8000      I= 1249  0.7366      I= 1349  2.1143
I= 1150  6.7759      I= 1200  3.7977      I= 1250  0.7370      I= 1350  2.1107
I= 1151  6.7784      I= 1201  3.7959      I= 1251  0.7494      I= 1351  2.1063
I= 1152  6.7609      I= 1202  3.7869      I= 1252  0.7568      I= 1352  2.1092
I= 1153  6.7307      I= 1203  3.7625      I= 1253  0.7439      I= 1353  2.0908
I= 1154  6.6423      I= 1204  3.6922      I= 1254  0.7226      I= 1354  2.0299
I= 1155  6.3764      I= 1205  3.5123      I= 1255  0.6898      I= 1355  1.9132
I= 1156  5.8354      I= 1206  3.1652      I= 1256  0.6477      I= 1356  1.7106
I= 1157  4.9536      I= 1207  2.6245      I= 1257  0.5751      I= 1357  1.4334
I= 1158  3.9205      I= 1208  2.0639      I= 1258  0.4779      I= 1358  1.1510
I= 1159  2.8987      I= 1209  1.5354      I= 1259  0.3921      I= 1359  0.8356
I= 1160  1.9735      I= 1210  0.9476      I= 1260  0.3106      I= 1360  0.5658
I= 1161  1.1476      I= 1211  0.4594      I= 1261  0.2180      I= 1361  0.3861
I= 1162  0.5161      I= 1212  0.1481      I= 1262  0.1893      I= 1362  0.2396
I= 1163  0.2270      I= 1213  0.0233      I= 1263  0.1658      I= 1363  0.1951
I= 1164  0.1668      I= 1214  0.0027      I= 1264  0.1785      I= 1364  0.1968
I= 1165  0.1775      I= 1215  0.0020      I= 1265  0.1990      I= 1365  0.1933
I= 1166  0.1889      I= 1216  0.0019      I= 1266  0.1690      I= 1366  0.1864
I= 1167  0.1718      I= 1217  0.0018      I= 1267  0.1723      I= 1367  0.1937
I= 1168  0.1929      I= 1218  0.0018      I= 1268  0.1843      I= 1368  0.1656
I= 1169  0.1916      I= 1219  0.0021      I= 1269  0.1743      I= 1369  0.1798
I= 1170  0.1832      I= 1220  0.0019      I= 1270  0.1778      I= 1370  0.1617

                             End of Scan
```

PEAK WIDTHS

PEAK TOPS

PEAK CENTERS

Figure 1. Field Control Step Scan
Input Value Ranges for Spectrum Evaluation and Program Parameters

TABLE I. Field Control System Data - Wt. %

I. A Listing of Control Runs - SRM 030

Run #	Date	U-234	U-235*	U-236	U-238*
	NBS Vol.	0.0187	3.0085	0.0202	96.9525
1	07-23-81	0.0186	3.0069	0.0195	96.9550
2	07-27-81	0.0189	3.0078	0.0201	96.9532
3	07-28-81	0.0187	3.0108	0.0202	96.9503
4	07-28-81	0.0188	3.0080	0.0205	96.9527
5	07-29-81	0.0181	3.0078	0.0206	96.9535
6	07-30-81	0.0183	3.0065	0.0204	96.9548
7	08-04-81	0.0190	3.0073	0.0207	96.9531
8	08-05-81	0.0185	3.0090	0.0204	96.9521
9	08-06-81	0.0184	3.0074	0.0206	96.9536
10	08-11-81	0.0188	3.0111	0.0205	96.9496
11	08-12-81	0.0190	3.0085	0.0204	96.9521
12	08-14-81	0.0194	3.0069	0.0205	96.9531
13	08-17-81	0.0191	3.0107	0.0200	96.9503
14	08-17-81	0.0184	3.0099	0.0212	96.9505
15	08-18-81	0.0187	3.0101	0.0206	96.9505
16	08-19-81	0.0186	3.0094	0.0205	96.9515
17	08-26-81	0.0188	3.0086	0.0208	96.9519
18	09-02-81	0.0188	3.0099	0.0207	96.9506
19	09-10-81	0.0181	3.0087	0.0203	96.9528
20	09-11-81	0.0183	3.0094	0.0200	96.9523
21	09-14-81	0.0190	3.0081	0.0197	96.9532
22	09-15-81	0.0183	3.0097	0.0205	96.9515
23	09-16-81	0.0185	3.0086	0.0210	96.9519
24	09-17-81	0.0188	3.0100	0.0201	96.9512
25	09-18-81	0.0189	3.0096	0.0203	96.9512
26	09-21-81	0.0190	3.0102	0.0199	96.9509
27	09-22-81	0.0187	3.0095	0.0202	96.9516
28	09-22-81	0.0189	3.0081	0.0204	96.9526

II. Summarized Data - Control SRM's

SRM		U-234	U-235*	U-236	U-238*
020	NBS Vol.	0.0123	2.0127	0.0164	97.9587
NBL Ave	N= 9	0.0119	2.0127	0.0164	97.9589
% RSD		5.1659	0.0450	2.8865	0.0015
030	NBS Vol.	0.0187	3.0085	0.0202	96.9525
NBL Ave	N= 28	0.0187	3.0089	0.0204	96.9521
% RSD		1.6787	0.0422	1.8035	0.0014
100	NBS Vol.	0.0666	10.0747	0.0376	89.8211
NBL Ave	N= 5	0.0665	10.0765	0.0380	89.8191
% RSD		0.5034	0.0510	2.0284	0.0056
970	NBS Vol.	1.6582	97.6625	0.1497	0.5296
NBL Ave	N= 4	1.6586	97.6613	0.1499	0.5302
% RSD		0.0788	0.0017	0.3129	0.1573

III. Sample With U-233

Run #	U-233	U-234	U-235	U-236	U-238
+1	0.0522	0.6449	60.0570	0.1915	39.0544
++2	0.0546	0.6444	60.0536	0.1903	39.0571

+1 30cm, 60deg. instrument, current control
++2 30cm, 90deg. instrument, field control

* Fourth decimal place is NBL best estimate

The range for the individual peak center values have been very consistent (<5 steps). Small changes have been attributed to an inability to accurately reset the accelerating voltage, changes in the room temperature, and possibly some differences in the sample to sample filament position. With the field control system under calculator control, progression towards a fully automated instrument is readily achievable through the use of stepping controls on the filament supply and the ion source focusing panel.

REFERENCES

1. E. L. Callis, NBL-289 (1979), p. 106.

2. V. E. Connolly, NBL-297 (1981), p. 14.

2. Development of a Fission Fragment Induced Desorption Mass Spectrometer for Isotope Ratio Analysis (W. H. Ulbricht, Jr.) Several further improvements have been made to the plasma-desorption time-of-flight mass spectrometer (TOFMS) described previously.[1] For its application to safeguards measurements, this instrument has been designed to examine isotope ratios, require almost no sample preparation, and has superior resolution/sensitivity to previous TOFMS. The addition of microchannel plate ion and fission fragment detectors has enhanced the resolution and sensitivity. The use of ^{252}Cf as a source of fission fragments to induce desorption, described last year, has also been shown to increase the sensitivity and greatly enhances the portability of the instrument.

The instrument is designed to examine untreated solid samples containing uranium. The sample is attached to a sample plate with a vacuum adhesive and placed in the unit for analysis. Because of the relative mildness of the desorption and ionization process, bond dissociation in the desorbed ions differs from other mass spectrometric ionization processes and offers the possibility of examining chemical species in the sample.

A topical report covering the construction, operation, and preliminary results obtained with the instrument is being prepared.

REFERENCE

1. W. H. Ulbricht, Jr., NBL-297 (1971), p. 23.

3. Correlations Between the Mass Discrimination Factors of Uranium and Plutonium (D. W. Crawford and M. A. Legel) Reliable measurements of the isotopic composition of plutonium materials by thermal ionization mass spectrometry require knowledge of the corrections necessary for mass discrimination and fractionation. Since adequately characterized plutonium isotopic standard reference materials (SRMs) are not currently available, uranium SRMs have been used for plutonium measurements. It has been assumed that both uranium and plutonium behave similarly during the ionization process. To verify this assumption, calibrated mixtures of ^{239}Pu and ^{242}Pu prepared by the Savannah River Plant (SRP) were analyzed by thermal ionization mass spectrometry.

The mixtures consisted of NBS SRM 949b (^{239}Pu = 98.05%) and SRP production metal 018A (^{242}Pu = 92.46%). The total plutonium content and isotopic composition of the stock solutions used for the mixture were determined independently. Weight aliquots of the stock solutions were mixed to yield nominal ^{242}Pu/^{239}Pu ratios of 0.1, 0.25, 1, 4, and 10, each with an uncertainty of about 0.10%. The mixtures were analyzed concurrently with a series of five NBS uranium isotopic standards of corresponding ^{238}U/^{235}U ratios. (See Table I.)

TABLE I

Plutonium and Uranium Ratio Values

Plutonium		Uranium	
SRP Mixture	R, $\frac{N_{Pu-242}}{N_{Pu-239}}$	NBS SRM	R, $\frac{N_{U-238}}{N_{U-235}}$
1	0.9144	U-500	1.00030
2	0.0859_2	U-900	0.09638
3	8.2903	U-100	8.80312
4	0.2436	U-800	0.23443
5	3.7071	U-200	3.97996

where: N = number of atoms of specific isotope

R = ratio of isotopes

All plutonium values as of January, 1981

Equal amounts of the uranium and plutonium were loaded onto rhenium filaments and analyzed. Ionizing filament temperature was maintained by $^{187}Re^+$ intensity monitoring and the total M^+ intensity of approximately 3 V (3×10^{-11} A) was the basis of sample filament temperature adjustment. Due to the greater ionization efficiency of plutonium over uranium, the target Pu^+ signal was achieved at a lower filament temperature than that observed for U^+. Critical parameters such as sample size, filament temperatures, intensities, operating vacuum pressure, and burn time during the analysis were carefully reproduced since these can affect the measurements obtained. These measurements were used to calculate the mass discrimination factors listed in Table II.

TABLE II

Mass Discrimination Factors for Plutonium and Uranium

(Average Burn time: 30 minutes)

Plutonium

SRP Mixture	R, Pu-242/Pu-239 obs.	RSD, %	n	$R_{calc.}/R_{obs.}$, $K_{242/239}$
1	0.91260	0.02	5	1.001971
2	0.08580	0.03	5	1.001357
3	8.27471	0.03	4	1.001884
4	0.24321	0.03	5	1.001590
5	3.70183	0.04	5	1.001423
			mean	1.001645

NBS SRM 947

R, Pu-240/Pu-239 cert.	R, Pu-240/Pu-239 obs.	RSD, %	n	$3\,[R_{cert.}/R_{obs.}-1] + 1$, $K_{242/239}$
0.24147	0.24133	0.03	5	1.001661

Uranium

NBS SRM	R, U-238/U-235 obs.	RSD, %	n	$R_{cert.}/R_{obs.}$, $K_{238/235}$
U-100	8.78559	0.04	4	1.001995
U-200	3.97357	0.03	4	1.001609
U-500	0.99851	0.03	6	1.001789
U-800	0.23405	0.04	4	1.001636
U-900	0.096239	0.01	5	1.001461
			mean	1.001698

where: K = mass discrimination factor

R = ratio of isotopes

n = number of filament loadings

To observe the fractionation pattern as a function of the rate of change of the correction per unit time, the correction vs. burn time values were plotted and an average slope for the filament loadings of each plutonium mixture and uranium standard was calculated, Table III.

TABLE III

Observed Fractionation Patterns of Plutonium and Uranium

Plutonium		Uranium	
SRP Mixture	Slope, $min.^{-1}$	NBS SRM	Slope, $min.^{-1}$
1	-3.0×10^{-5}	U-100	-2.3×10^{-5}
2	-3.2×10^{-5}	U-200	-3.3×10^{-5}
3	-2.8×10^{-5}	U-500	-3.7×10^{-5}
4	-4.7×10^{-5}	U-800	-4.0×10^{-5}
5	-3.0×10^{-5}	U-900	-3.6×10^{-5}
mean	-3.3×10^{-5}	mean	-3.6×10^{-5}

The evaluation of the data from this study indicates that, in the thermal ionization process, the fractionation and the mass discrimination corrections for uranium and plutonium are similar. Uranium reference materials appear to be satisfactory for application to plutonium measurements within the stated experimental uncertainty. More accurate estimates of the corrections for mass discrimination, required to place plutonium isotopic RMs on an absolute basis rather than relative to uranium, are dependent upon a reduced uncertainty in prepared ratios of $^{242}Pu/^{239}Pu$. A program involving blending of solutions of carefully certified separated isotopes is to be undertaken in FY 1982 by NBL and NBS.

III. STANDARDS AND REFERENCE MATERIALS

A. NBL STANDARDS AND REFERENCE MATERIALS

1. Status of the NBL Reference Material Program (N. M. Trahey and L. E. Budzichowski) During this report period, 866 NBL Certified Reference Material (CRM) units were sold to USA and non-USA customers. The types and

numbers of each CRM actually distributed are itemized in Table I. A total of 15 U.S. NRC licensees, 4 U.S. DOE contractors, and 9 private domestic facilities ordered CRMs, as did 15 non-USA laboratories.

Customer demand was again greatest for those CRMs used to calibrate and/or verify safeguards accountancy and radiometric measurement processes. Specific to safeguards applications, the CRMs frequently requested were NBL CRM No. 97 Uranium (low enriched) Oxide - UO_2, NBL CRM No. 98 (1-7) Impurities in Uranium (normal) Oxide - U_3O_8, NBL CRM No. 113 Uranium (low enriched) Hexafluoride - UF_6, and NBL CRM No. 114 Uranium (normal) Oxide - U_3O_8. For radiometric measurements of U and Th ore-bearing materials and preparation of sources for field nondestructive assay (NDA) measurement uses, the CRMs frequently requested were NBL CRM No. 7-A Monazite Sand, NBL CRM Nos. 101-A through 105-A Pitchblende Ore (diluted), and NBL CRM Nos. 106-A through 110-A Monazite Sand (diluted).

By mid FY 81, all available stock of NBL CRM No. 98 (1-7) U_3O_8 had been sold. Plans to replace it were implemented and are reported elsewhere.[1]

Characterization and certification of NBL CRM No. 121 Uranium (depleted) Oxide - UO_2 impurity standard[2], NBL CRM No. 122 Plutonium Oxide - PuO_2 assay and isotopic standard, and NBL CRM No. 125 Uranium (enriched) Oxide - UO_2 pellet assay and isotopic standard[3] are in process and these CRMs should be made available for purchase within the next reporting period.

The 1982 Edition of the NBL Certified Reference Material Catalog was prepared for publication and replaces the NBL 1978 - 1979 Price List. Detailed ordering instructions and shipping information reflecting current U.S.A. and international regulations covering domestic and foreign purchases of NBL CRMs are included in the Catalog, along with technical descriptions for each CRM category, and CRM unit prices and availability. Copies of the catalog can be obtained from NBL.

TABLE I

NBL Reference Material Sales Fiscal Year 1981

(10-01-80 thru 09-30-81)

NBL CRM No.	Desciption	Number of Units Sold To Domestic	Foreign	Total
1-A	Phosphate Rock	01	00	01
3-B	Pitchblende Ore	04	02	06
4	Carnotite Ore	27	00	27
5	Carnotite Ore	15	00	15
6-A	Pitchblende Ore	11	06	17
7-A	Monazite Sand	385	08	393
17-B	UF4	00	00	00
18	U03	01	00	01
42(1-7)	Pitchblende Ore	11	05	16
66(1-7)	Th02	00	01	01
74-A	Pitchblende Ore	01	02	03
79-A	Monazite Sand	01	00	01
80-A	Monazite Sand	00	02	02
82-A	Monazite Sand	02	02	04
85	Beryllium Metal	24	00	24
86	Beryllium Metal	00	00	00
87	Beryllium Metal	00	00	00
88	Beryllium Metal	12	00	12
96(1-6)	Beryllium Oxide	00	01	01
*97	U02	20	21	41
98(1-7)	U308	55	19	74
101	Pitchblende Ore	01	05	06
101-A	Pitchblende Ore	02	01	03
102	Pitchblende Ore	03	06	09
102-A	Pitchblende Ore	03	01	03
103-A	Pitchblende Ore	04	00	04
104	Pitchblende Ore	00	02	02
104-A	Pitchblende Ore	06	00	06
105	Pitchblende Ore	00	00	00
105-A	Pitchblende Ore	05	10	15
106	Monazite Sand	04	07	11

106-A	Monazite Sand	04	01	05
107	Monazite Sand	02	03	05
107-A	Monazite Sand	02	01	03
108-A	Monazite Sand	03	01	04
109	Monazite Sand	02	11	13
109-A	Monazite Sand	02	00	02
110	Monazite Sand	01	00	01
110-A	Monazite Sand	02	00	02
112	U Metal Chips	00	06	06
*113	UF6	64	00	64
114	U308	40	01	41
115	Depleted U Metal	02	04	06
*116	Enriched U Metal	00	00	00
*117	U Isotope Mixture	00	01	01
*118	BISO Beads	07	00	07
*119	TRISO Beads	08	00	08
*120	UO2	00	00	00
F226	Beryllium Metal	03**	00	04
F227	Beryllium Metal	10**	00	08
F229	Silica Dunite	05**	00	04
	Totals	736	130	866

* = Enriched Uranium

** = Not included in total units sold

REFERENCES

1. P. M. Santoliquido, NBL-304 (1982), p. 43.

2. W. Nichiporuk, NBL-304 (1982), p. 42.

3. K. Scheidelman, NBL-304 (1982), p. 41.

2. Certification of NBL UO_2 Pellet Reference Material (CRM No. 125)

(K. Scheidelman) Uranium dioxide (UO_2) pellets acquired as a Department of

Energy excess material are being certified as an NBL reference material for uranium assay and isotopic composition. The certification is being carried out on 14 randomly selected pellets. Uranium assay results are being obtained by gravimetry (corrected for impurities by emission spectrography) and by titrimetry. Titrimetric assay using a weight titration technique is being performed directly on dissolved portions of the UO_2 and also on UO_2 portions that have been ignited to U_3O_8. All titrations are being done concurrently with uranium standards.

3. Determination of Impurities in UO_2 Reference Material (CRM No. 121)

(W. Nichiporuk) In order to meet the safeguards needs for a certified uranium spectrographic impurity reference material identified by field offices and contractors in 1978, the New Brunswick Laboratory procured one lot of high purity depleted uranium dioxide which was prepared and packaged for issuance. Labeled NBL CRM No. 121 UO_2, this new oxide is of a high degree of homogeneity and particle size and is suitable for the preparation of the typical very small samples required for spectrographic impurity measurement validation or calibration.

About 16 kilograms of the material were received from the Westinghouse Electric Corporation with a specified particle size range and chemical composition. The material was stored in 2-kg batches. Rather than micropulverizing the whole lot to a predetermined particle size range, the fraction of the material which would not pass through a 140-mesh screen was excluded. This procedure was based on the initial exploratory impurity homogeneity studies performed at this laboratory which showed no discernable relationship between particle size and impurity content. Each 2-kg batch of the material was sieved, and the fractions passing through 140-mesh screen were combined, mixed in a V-blender, and packaged into 393 25-g units.

The New Brunswick Laboratory sampling and analysis procedure developed for the impurity determinations in CRM No. 121 is given below. A packaged unit of the material (i.e., 25 g) is dissolved with distilled concentrated HNO_3 in a Teflon beaker, evaporated to dryness, redissolved in $8\underline{N}$ HNO_3 and diluted to 50 mL with this acid. From this solution the matrix uranium is extracted with 100% tributyl phosphate, while major impurity elements remain in the acidic aqueous phase. Only about 10 micrograms of residual matrix uranium per gram were found to be left in the aqueous phase allowing only minimal interferences in the present method of impurity determination.

One packaged unit of CRM No. 121 is dissolved and extracted by the above procedures to make up one spectrographic analysis sample, whereas two packaged units of the oxide are dissolved and extracted individually, then combined to form one atomic absorption analysis sample. Some 15 impurity elements which do not extract into tributyl phosphate and which have satisfactory emission lines and atomic absorption resonance lines in the wave-length region of 250 to 380 nm are being determined in the present program. A set of three reference materials, NBL CRM No. 98 (4-6) U_3O_8, with certified impurity contents and in which impurities are repeatedly determined in different laboratories, is being used to check the effect of the method on impurities.

To date, in accordance with a statistical analysis plan, seven emission spectrographic and five atomic absorption analysis samples have been prepared. Impurity determinations are in progress.

4. Design of Replacements for NBL Uranium Spectrographic Reference Material (CRM No. 98) (P. M. Santoliquido) NBL has provided a U_3O_8 spectrographic impurity standard since 1957. CRM No. 98 (1-7), which contains 30 trace elements at seven concentration levels, represents the third generation of this standard. This CRM is widely used by DOE contractors and NRC licensees, as well as many non-USA laboratories, in safeguards analytical work. During FY 1980, it ranked third in total sales of all reference materials provided by NBL.[1] Because of the unexpected exceptionally high demand for this CRM, NBL inventories have been rapidly depleted and during this reporting period the supply of CRM No. 98 (1-7) was exhausted, prematurely necessitating an accelerated replacement schedule.

The trend in the composition of the successive generations of this impurity standard has been to increase the number of trace elements. Thus, CRM No. 65 (1-5) had 12 trace elements; CRM No. 95 (1-7) had 22; CRM No. 98 (1-7) had 30. While the additional elements have increased the usefulness of each succeeding reference material, it has also produced two undesirable effects: first, the total concentration of added impurities has become so great that the matrix has become less of a match for high purity samples; and, secondly, the amount of technical effort required to prepare and certify replacements has increased to 4-6 staff-years. A need for a change in design to extend the usefulness of the CRM and conserve its inventory life was therefore clearly indicated.

In order to determine which of the 30 trace elements could be eliminated without seriously decreasing the usefulness of the reference material, 20 USA and 11 non-USA purchasers of the material were queried. Fifty-five percent of both the USA and non-USA groups replied. Using the information thus gathered, the 30 elements were divided into three groups according to frequency of usage. The high-use group, which was always used by more than 76% of those replying, consisted of aluminum, boron, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, silicon, tin, vanadium, and zinc. The moderate-use group, which was always used by 47-59% of those replying, consisted of beryllium, bismuth, cobalt, silver, sodium, and titanium. The low-use group, which more than 23% of those replying reported they never used, consisted of antimony, barium, indium, lithium, phosphorus, potassium, strontium, and tungsten. It was therefore decided to eliminate all of the low-use group elements with the exception of tungsten. Specific requests regarding concentrations were received for tungsten, which indicated that, for those who do determine it, it is an important element.

Two replacements are planned for CRM No. 98 (1-7): CRM No. 123 (1-7), which will be an 18-element standard; and CRM No. 124 (1-7), which will be a 24-element standard. The 18-element standard will contain the 16 elements of the high-use group plus zirconium and sodium. Zirconium is being added because there is sufficient interest in this element to warrant its inclusion. Sodium is being included because it is present in the compounds to be used for adding silicon, tungsten, and tin to the U_3O_8 base. The 24-element standard will contain all the elements in the 18-element standard plus the moderate-use group elements and tungsten. The concentrations planned are shown in Table I.

TABLE I

Plan For Added Impurities in Spectrographic Reference Materials

Elements	Concentration Levels, Values in ug/g U						CRM No.
	1	2	3	4	5	6	
Al, Ca, Fe, Ni, Si, Zn, Zr	200	100	50	20	10	5	123 & 124
Cr, Mg, Mo	100	50	20	10	5	2	123 & 124
Cu, Mn, Pb, Sn, V	50	25	10	5	2.5	1	123 & 124
B, Cd	5.0	2.5	1.0	0.5	0.25	0.1	123 & 124
W	200	100	50	20	10	5	124 only
Bi, Ti	50	25	10	5.0	2.5	1.0	124 only
Be, Co	25	12.5	5.0	2.5	1.25	0.5	124 only
Ag	5.0	2.5	1.0	0.5	0.25	0.1	124 only
Na	Dependent on Si, Sn, W						123 & 124

CRM No. 123 (1-7) and CRM No. 124 (1-7) will be prepared and certified concurrently. Preparation will be by the same general method used for CRM No. 98 (1-7); this is, the addition of solution pools to a dry base with subsequent mixing, drying, and blending.[2] Work is now in progress and will continue throughout FY 1982.

REFERENCES

1. N. M. Trahey and L. E. Budzichowski, NBL-297 (1981), p. 27.

2. C. G. Goldbeck and L. J. Pinto, NBL-297 (1974), p. 58.

5. Investigation of a Uranium Dioxide Bead Material for NBL Reference Material and Evaluation Program Uses (N. M. Trahey) In a continuing search for satisfactory candidate reference materials for UO_2 assay and isotopic measurement calibration and verification purposes, a UO_2 bead fuel fabrication project based on gel-supported precipitation was examined. In this process used by General Atomic Company (GAC), uranium broth, prepared from uranyl nitrate combined with complexing and gelling agents, is injected into an ammonia column to produce spherodized particles which are subsequently sintered into UO_2 beads. Throughout this process the chemical and physical specifications of the particles are rigorously controlled to provide a product of uniformly high quality. Furthermore, because the beads are sintered at 1650°C, they resist moisture degradation more effectively than do low-fired UO_2 powders used in the fabrication of commercial reactor fuels. For these reasons, it was proposed that these beads should be evaluated as a candidate reference material.

At NBL's request, GAC provided 90 grams of depleted UO_2 beads for study and evaluation. The material was tested for acid dissolution characteristics, moisture pickup under ambient conditions, and uranium content. In the acid dissolution studies, a variety of acids and acid mixtures were employed to ascertain the best technique for achieving total dissolution of the beads. Two mixtures, HNO_3-H_2SO_4 and HNO_3-HF, were found to be suitable for dissolving the beads in a timely manner. The uranium contents of three samples dissolved in HNO_3-H_2SO_4 and two dissolved in HNO_3-HF were determined by the NBL modified titrimetric method. The results obtained showed no significant differences between the two acid mixtures used a mean Wt.% U value for the beads of $88.007_4 \pm 0.008_4$ ($\bar{x} \pm s_{\bar{x}}$, n = 5) was established. From the small uncertainty in the mean value it can be inferred that either acid mixtures was suitable for dissolution and that the bead material, as sampled, is homogeneous in uranium content.

Moisture tests were also conducted on the beads by periodically weighing measured quantities of beads which were constantly exposed to laboratory atmospheric conditions. Four 0.5-gram samples were weighed a total of five times in a three-month period. During this period, laboratory temperatures and humidities ranged from $24^{o}C$ to $26^{o}C$ and from 60% to 76%, respectively. The average cumulative mass gain per sample for the entire period was $+0.052_9\%$. This gain is a considerable improvement over that which normally occurs in low-fired UO_2 and gives a reasonable indication of the expected long-term stability of the beads especially when properly packaged as a reference material.

The results of high precision assay tests on the beads remain to be evaluated. However, those measurements obtained to date, coupled with the test results described above, are evidence that this UO_2 will be very useful as a reference material. Efforts to obtain kilogram quantities of the sintered beads at an enrichment of 3 wt.% ^{235}U are now proceeding.

6. Certification of NBL Uranium Counting Standards (A. M. Voeks) Five low-level uranium counting standards (NBL CRM Nos. 101-A through 105-A) were prepared as previously described.[1] Certification of the materials was begun during the last report period[2] and is currently complete. The analysis procedure, an Arsenazo III spectrophotometric method, is detailed in the Certification Plan.[3] Certified values are shown in Table I.

TABLE I

Certified Values for NBL CRM Nos. 101-A to 105-A

NBL CRM	Certified Value (%U ± 95% C.L.)
101-A	$1.007_3 \pm 0.013_6$
102-A	$0.1025_3 \pm 0.0019_8$
103-A	$0.0499_2 \pm 0.0007_8$
104-A	$0.00988_7 \pm 0.00020_3$
105-A	$0.00102_3 \pm 0.00002_3$

REFERENCES

1. R. D. Peavy and K. S. Scheidelman, NBL-293 (1980), p. 53.

2. A. M. Voeks and K. S. Scheidelman, NBL-297 (1981), p. 30.

3. Certification Plan for Uranium Counting Standards NBL Reference Materials 101-A to 105-A.

7. Certification of Prototype NDA Reference Materials (A. M. Voeks) The New Brunswick Laboratory has designed an interlaboratory comparison program to evaluate the capabilities of participating laboratories for the measurement of scrap and waste materials.[1] Three prototype materials: ion exchange resin,[2] cellulose fiber,[2] and synthetic calcined ash,[3] were prepared previously and their certification has been completed.

The ion exchange resin was certified according to the described plan.[4] Samples were weighed into disposable ion exchange columns and the uranium eluted from the resin with 0.1N HCl. After treatment to remove the chloride ion, the samples were analyzed by the NBL titrimetric method for uranium. Titration data from uranium standards treated in the same manner were used to correct for any retention of uranium on the resin.

The cellulose fiber was certified according to the described plan.[5] Samples were weighed into platinum dishes, ignited to remove the cellulose, transferred to beakers, and assayed for uranium by the NBL titrimetric method.

The synthetic calcined ash was analyzed by three different methods: mineral acid decomposition,[6] sodium fluoride-pyrosulfate transposition fusion,[7] and sodium carbonate fusion. In the mineral acid decomposition method, weighed samples were boiled with aqua regia, fumed repeatedly with $HClO_4$ and HF, transferred to platinum dishes, heated to dryness, fumed repeatedly with HNO_3 and HF, transferred to beakers, heated overnight with H_3PO_4, and assayed for uranium as before. In the sodium fluoride-pyrosulfate transposition method, weighed samples were heated to dryness with HF in platinum crucibles, fused with NaF, cooled and carefully heated with H_2SO_4

until transposition to a burgundy-colored melt occurred. The melts were dissolved in dilute $HClO_4$, then the solutions were filtered and assayed for uranium. The absence of uranium in the residues left on the filter papers was confirmed by nondestructive assay. In the sodium carbonate fusion method, weighed samples were fused with Na_2CO_3-$NaNO_2$ in platinum crucibles, and the melts were dissolved in dilute HNO_3. The solutions were evaporated to dryness, the residues were redissolved in H_3PO_4-HNO_3-$HClO_4$, and the resulting solutions were heated to $HClO_4$ fumes. After the addition of water, the solutions were evaporated to a specified volume, a small amount of HF was added, and the solutions were assayed for uranium.

Since these prototype materials are currently being used in an evaluation program,[8] their certified values cannot be published at this time.

REFERENCES

1. A. M. Voeks, NBL-293 (1980), p. 62.
2. A. M. Voeks, NBL-292 (1979), p. 53.
3. A. M. Voeks, NBL-293 (1980), p. 50.
4. Certification of Resin Prototype NDA Reference Material, August, 1979.
5. Certification of Cellulose Prototype NDA Reference Material, August, 1979.
6. Certification of Synthetic Calcined Ash Prototype NDA Reference Material, August, 1979.
7. C. R. Balulescu, NBL-297 (1981), p. 10.
8. A. M. Voeks, NBL-304 (1982), p. 56.

8. Preparation and Certification of Uranium Reference Solutions for the Nuclear Regulatory Commission (A. M. Voeks) As part of the safeguards evaluation of the measurement capabilities of nuclear fuel facilities,

regional offices of the U.S. Nuclear Regulatory Commission (NRC) periodically require certified uranium reference solutions. Region III requested two uranium reference solutions, both containing iron and nickel and one also containing silicon. The requested concentrations of uranium, iron, and nickel had to be reduced by 50% and the silicon eliminated due to solubility constraints. Both solutions were prepared by dissolving NBL uranium (normal) metal, ferric nitrate heptahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] and nickelous nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] in 2-3N HNO_3. The uranium concentrations of these solutions were verified using the NBL titrimetric method for uranium. Eight bottles of each of the two solutions, each containing approximately 25 mL of solution, were prepared to contain 14% U, 3% Fe, 1.7% Ni, and 23.8% U, 0.26% Fe, 0.01% Ni, respectively.

In response to a request from Region I for three uranium reference solutions, NBL uranium (normal) metal was dissolved in minimal quantities of nitric acid to provide solutions containing 5, 7, and 9 mg U/g solution, respectively. The uranium concentrations of these solutions were verified as before. Twenty bottles of each solution, each containing approximately 45 mL of solution, were prepared.

B. NBS REFERENCE MATERIALS

1. Transfer of NBS Nuclear SRM Distribution Activities to NBL (N. M. Trahey and T. E. Gills*) Recent revisions in the requirements of the National Bureau of Standards (NBS) nuclear license and subsequent decreased storage capacity for special nuclear materials (SNM) at its Gaithersburg, MD, site, have caused NBS to transfer all SNM Standard Reference Materials (SRMs) to NBL. Selection of NBL as the future storage and distribution site for NBS nuclear SRMs was made because of available NBL facilities and a coexisting nuclear reference materials program. In addition to transferring physical possession and responsibility for the storage, accountability, and distribution of its Special Nuclear SRM inventory to NBL, the NBL will assume responsibility for future Special Nuclear SRM preparation and certification

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*Address: Office of Standard Reference Materials, U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20234 efforts, except in cases involving unique technical considerations. As supplies of NBS Special Nuclear SRMs are exhausted, NBL will also prepare and certify new/replacement materials to fill measurement needs. These new materials will be issued as NBL Certified Reference Materials (CRMs).

The Interagency Agreement, prepared and signed during this reporting period, established October 1, 1981, as the date upon which transfer of Special Nuclear SRM responsibilities from NBS to NBL would become effective. Accordingly, NBS notified its customers of the impending transfer and provided a status report of the SRMs involved.[1] Table I describes the SRMs to be distributed by NBL and lists unit prices and availabilities.

The transfer process was coordinated between NBL and NBS in a manner intended to minimize disruptions in services to Special Nuclear SRM customers. The most important changes which had to be instituted were in (1) the approval process followed for non-USA purchases of SRMs, and (2) financial accounting/invoicing of the individual orders received. To inform and explain these changes to SRM customers, NBS will issue a memorandum with detailed ordering instructions.

REFERENCE

1. T. E. Gills, NBS/OSRM Memorandum for Purchasers of NBS Special Nuclear Materials, August 26, 1981.

TABLE I

NBS Special Nuclear Standard Reference Materials (SRMs) To Be Distributed by NBL as of October 1, 1981

SRM #	Description	Unit Size (in grams)	Unit Price (in U.S. dollars)	Comments
U-0002	U_3O_8, depleted - 0.02 At.% ^{235}U	1.2	178	Available Now
U-005	U_3O_8, depleted - 0.5 At.% ^{235}U	1.2	-	Available Jan., 1983
U-010	U_3O_8, enriched - 1.0 At.% ^{235}U	1.2	175	Available Now
U-015	U_3O_8, enriched - 1.5 At.% ^{235}U	1.2	175	Available Now
U-020	U_3O_8, enriched - 2.0 At.% ^{235}U	1.2	176	Available Jan., 1983
U-030	U_3O_8, enriched - 3.0 At.% ^{235}U	1.2	-	Available Jan., 1983
U-050	U_3O_8, enriched - 5.0 At.% ^{235}U	1.2	176	Available Now
U-100	U_3O_8, enriched - 10.0 At.% ^{235}U	1.2	177	Available Now
U-150	U_3O_8, enriched - 15.0 At.% ^{235}U	1.2	178	Available Now
U-200	U_3O_8, enriched - 20.0 At.% ^{235}U	1.2	178	Available Now
U-350	U_3O_8, enriched - 35.0 At.% ^{235}U	1.2	181	Available Now
U-500	U_3O_8, enriched - 50.0 At.% ^{235}U	1.2	184	Available Now
U-750	U_3O_8, enriched - 75.0 At.% ^{235}U	1.2	188	Available Now
U-800	U_3O_8, enriched - 80.0 At.% ^{235}U	1.2	189	Available Now
U-850	U_3O_8, enriched - 85.0 At.% ^{235}U	1.2	190	Available Now
U-900	U_3O_8, enriched - 90.0 At.% ^{235}U	1.2	191	Available Now
U-930	U_3O_8, enriched - 93.0 At.% ^{235}U	1.2	192	Available Now
U-970	U_3O_8, enriched - 97.0 At.% ^{235}U	1.2	188	Available Now
945	Plutonium Metal	5	462	Available Now
946	$Pu(SO_4)_2 \cdot 4H_2O$	0.53	255	Available Now
947	$Pu(SO_4)_2 \cdot 4H_2O$	0.53	256	Available Now
948	$Pu(SO_4)_2 \cdot 4H_2O$	0.53	190	Available Now
949f	Plutonium Metal			
950b	U_3O_8, normal	25	172	Available Now
960	Uranium Metal, normal	26	179	Available Now
993	Uranium Nitrate Solution, 99.8 At.% ^{235}U	15	188	Available Now
995	Uranium Nitrate Solution, 99.9 At.% ^{233}U	10	172	Available Now
996	Plutonium Sulfate, dried-97.9 At.% ^{244}Pu	(0.001 Pu)	325	Available Now

IV. EVALUATION PROGRAMS

A. SAFEGUARDS ANALYTICAL LABORATORY EVALUATION (SALE) PROGRAM

1. Safeguards Analytical Laboratory Evaluation (SALE) Program (B. W. Moran) The Safeguards Analytical Laboratory Evaluation (SALE) Program provides a mechanism through which the measurement capabilities of the participating laboratories may be evaluated and the quality of nuclear materials measurements improved. The SALE Steering Committee during its July, 1981, meeting recommended the following revision to program objectives:

1) To estimate the measurement capability of participating laboratories to routinely assay special nuclear materials in the nuclear fuel cycle for uranium and plutonium and their fissile isotope content.

2) To establish a scientifically valid body of measurement data which can be used to quantitatively assess or define routinely achievable measurement capability.

3) To provide a medium for the comparison and dissemination of nuclear materials measurement technology that encourages improvement in measurement performance.

The Steering Committee recommended that the SALE Program should begin to (1) investigate the inclusion of scrap and waste materials in the normal sample distribution and (2) make more definitive statements concerning the capabilities of methods used for the analysis of the SALE materials. Recommendations were also made concerning increased information that should be conveyed through the SALE Program Annual Report.

The annual report distributed during June, 1981, summarized and evaluated all data received during the 1980 calendar year. The report included a summary of program activities, a discussion of the statistical methods employed in evaluating the data, and a discussion of the statistically evaluated data. The report was distributed during the month preceeding the program participants meeting, thereby allowing most attendees to review and evaluate the data prior to the meeting.

The Fourth SALE Program Participants Meeting was held during July, 1981, on the Argonne National Laboratory (Illinois) site. The two day meeting was attended by 62 persons representing 32 organizations, including 7 non-U.S. laboratories. Presentations the first day of the meeting covered the administration of the SALE Program and new methods applicable to the safeguards of nuclear materials. The second day, discussions of methods in use for the analysis of program materials were stressed. A total of 25 presentations were made. All presentations and the edited discussions following the presentations have been compiled for distribution to participants in the "Minutes of the Fourth SALE Program Participants Meeting" report for distribution during October, 1981.

There are currently 49 active participants in the SALE Program: 27 from the U.S. and 22 from outside of the U.S. Three new participants joined the program during 1981.

All sample shipments scheduled for fiscal year 1981 were made with the exception of plutonium shipments to Japan and Czechoslovakia. Approval has been received for plutonium shipments to Czechoslovakia during 1982. Procedures are being investigated to minimize the high cost of shipping Type B quantities of plutonium into Japan. An agreement has been reached with the Central Bureau for Nuclear Measurements (CBNM), Geel, Belgium, whereby future plutonium shipments to EURATOM facilities will be consolidated into one shipment to be redistributed by CBNM. The IAEA has requested that shipments to Czechoslovakia be routed through the Seibersdorf Laboratory. These agreements will decrease the number of plutonium shipments to Europe from seven to two annually. All shipments have now been placed on an annual basis and are being made near the beginning of each calendar year.

Four materials are being distributed in the program: uranyl nitrate solutions (4 lots), uranium dioxide powder (1 lot), plutonium dioxide powder (1 lot), and plutonium-uranium mixed oxide pellets (1 lot). Three new lots of plutonium dioxide powder (high fired, 1250°C) were received from Los Alamos

National Laboratory and a characterization plan for their certification has been developed. The characterization of the uranium dioxide pellets to be distributed in 1982 is in progress.

Six bimonthly data reports are published annually. These reports graphically and numerically summarize all data from the analysis of the four SALE materials received during the 12 months preceeding the preparation of the report.

B. GENERAL ANALYTICAL EVALUATION (GAE) PROGRAM

1. General Analytical Evaluation (GAE) Program (B. W. Moran) The principal objective of the General Analytical Evaluation (GAE) Program is the evaluation of measurement performance on input material for enriched uranium scrap recovery operations. Six samples are distributed for monthly analysis: three synthetic dissolver solutions (low enriched), one production dissolver solution (high enriched), and two uranium oxide powders (normal). Each of the four solutions is assayed by the participants to determine the uranium concentration and ^{235}U abundance; the oxide powders are analyzed for non-volatile impurities. Measurements are reported in duplicate and are tabulated after all data for a monthly sample are received. Monthly reports are then issued comparing the reported measurements with either the verified prepared value or the monthly average of the participants' data. Data are coded to preserve anonymity.

Four lots of each synthetic dissolver solution were prepared and verified. The three synthetic matrices were uranyl nitrate solutions, uranium-impurities (Fe, Al, Ni, Cr, Cu) solutions, and uranium-stainless steel (Fe, Ni, Cr) solutions. Three new lots of production dissolver solutions acquired from Oak Ridge National Laboratory were filtered and bottled. The uranium oxide powders were selected or prepared from NBL CRM Nos. 18, 112, and 114. Four of the seven participants analyze all six materials, two analyze all except the high-enriched production dissolver solutions, and one participant analyzes only the uranyl nitrate solutions and the uranium oxide powders. Sample shipments are made quarterly.

In July, 1981, the GAE Program participants met at NBL to discuss new directions for the Program. It was decided to continue the program because of the benefits received by the participants although most materials of interest had been evaluated. Recommendations made by the participants for future sample materials were: (1) an impure U_3O_8 material for assay, (2) samples enriched to less than 5% ^{235}U only, and (3) oxide samples for impurity analysis containing low levels of Fe, Ni, and Al with total impurity levels of less than 1%.

C. OTHER EVALUATION PROGRAMS

1. NDA Prototype Reference Materials Evaluation Program (A. M. Voeks) The measurement phase of the NBL NDA Reference Materials Program for the evaluation of the measurement capabilities of participating laboratories for scrap and waste materials previously described[1,2] has continued. There are 18 organizations participating, including three non-U.S. participants. As of September, 1981, the materials were undergoing measurements by the twelfth participant and results were received from seven participants. Since it is anticipated that circulating the reference materials to the non-U.S. participants will take an extended period of time, an interim report will be issued after the domestic participants have completed their measurements.

REFERENCES

1. A. M. Voeks, NBL-293 (1980), p. 62.

2. N. M. Trahey, A. M. Voeks, NBL-297 (1981), p. 35.

2. Evaluation of the Los Alamos L_{III}-Edge Densitometer (W. J. McGonnagle, M. K. Holland, C. S. Reynolds and A. C. Zook) The Los Alamos National Laboratory L_{III}-Edge Densitometer has been under evaluation at NBL since November, 1980, in order to fully define its operating parameters and scope of application.[1] The specific goals of this evaluation were to: (a) determine the precision and accuracy of the system, (b) determine the effect of matrix contaminants with low, intermediate, and high atomic number on the precision and accuracy, (c) develop calibration curves for this system by

making measurements of uranium and plutonium in separate and mixed solutions prepared from well-characterized materials, and (d) determine the concentrations of synthetic or typical fuel cycle materials.

As of this report period L_{III}-edge measurements and chemical analyses have been completed on: (a) uranium samples containing approximately 5, 20, 35, 50, 65 and 80 g U/L, (b) plutonium samples containing approximately 2.5, 5, 20, 35, 50 and 65 g Pu/L, and (c) mixed solutions as shown in Table I.

TABLE I

Uranium-Plutonium Solutions

U-Pu, g/L	U/Pu Ratio
5	1:1
20	2:1
35	3:1
50	5:1
50	3:1
65	2:1
80	2:1

Upon completion of measurements on some special solutions to test the effects of matrices, acid concentration, and the presence of hydroxylamine, a complete topical report of the evaluation study will be prepared.

REFERENCE

1. W. J. McGonnagle, P. Russo, J. Sprinkle, N. M. Trahey, J. M. Scarborough, NBL-297 (1981), pp. 37-38.

V. REPORTS AND PRESENTATIONS

T. L. Frazzini, M. K. Holland, J. R. Weiss, and C. E. Pietri, "Corrections of Systematic Error from Analog Integration in Controlled-Potential Coulometry", Analytical Chemistry 52, 2112 (1980).

M. K. Holland, T. L. Frazzini, B. P. Freeman, J. R. Weiss, and C. E. Pietri, "A System for the Analysis of Plutonium Using Ion-Exchange Purification and Controlled-Potential Coulometry", presented at the Plutonium Exchange Meeting, November 12-14, 1980, Sacramento, CA.

A. C. Zook and C. E. Pietri, "Determination of Uranium in Plutonium by Laser Fluorometry", presented at the Plutonium Exchange Meeting, November 12-14, 1980, Sacramento, CA.

M. K. Holland, J. R. Weiss, and C. E. Pietri, "A Reference Method for the Determination of Plutonium Using Controlled-Potential Coulometry", presented at the 3rd ESARDA Symposium, May 6-8, 1981, Karlsruhe, Germany.

J. M. Scarborough and N. M. Trahey, "Evaluation of an Interlaboratory Program on Chemical and Nondestructive Measurements of HTGR Fuel Materials", accepted but not presented at the 3rd ESARDA Symposium, May 6-8, 1981, Karlsruhe, Germany.

W. J. McGonnagle, M. K. Holland, C. S. Reynolds, N. M. Trahey, and A. C. Zook, "Evaluation of the LASL L_{III}-Edge Densitometer", presented at the 4th International Conference on Nondestructive Evaluation in the Nuclear Industry, May 25-29, 1981, Lindau, Germany.

D. W. Crawford and M. A. Legel, "Correlations Between the Mass Discrimination of Uranium and Plutonium", presented at the 29th Annual Conference on Mass Spectrometry and Allied Topics, May 25-28, 1981, Minneapolis, MN.

K. Lewis, editor, "Progress Report for the Period October 1979 through September 1980", NBL-297, April, 1981.

B. W. Moran, editor, "Safeguards Analytical Laboratory Evaluation (SALE) 1980 Annual Report", NBL-300, June, 1981.

A. C. Zook, N. M. Trahey, and W. J. McGonnagle, "Application of a Chemical Calibration Protocol to the Evaluation of a Nondestructive Assay System", presented at the 22nd Annual Meeting of the Institute for Nuclear Materials Management, July 13-15, 1981, San Francisco, CA.

M. K. Holland, J. R. Weiss, and C. E. Pietri, "The NBL Controlled-Potential Coulometric Method for the Determination of Plutonium", NBL-299, June, 1981.

R. E. Toohey, C. G. Cacic (NBL), R. D. Oldham, and R. P. Larsen, "The Concentration of Plutonium in Hair Following Intravenous Injections", Health Physics 40, 881 (1981).

C. E. Pietri, "The Analytical Chemist as a Human Resource", presented at the 30th Annual Meeting of the American Chemical Society, August 25-28, 1981, New York, NY.

T. L. Frazzini, M. K. Holland, J. R. Weiss, and C. E. Pietri, "A Digital Integrator for Controlled-Potential Coulometry", Analytica Chimica Acta 129, 125 (1981).

C. E. Pietri, J. R. Weiss, and B. P. Freeman, "The Quantitative Ion Exchange Separation of Plutonium from Impurities", NBL-298, September, 1981.

A. C. Zook, L. H. Collins, and C. E. Pietri, "Determination of Nanogram Quantities of Uranium by Pulsed-Laser Fluorometry", Mikrochim. Acta (Wien), 1981 II, 457 (1981).

U.S. Patent No. 4,2444,800: "Apparatus for Use in Rapid and Accurate Controlled-Potential Coulometric Analysis", issued January 13, 1981, has been awarded to T. L. Frazzini, M. K. Holland, C. E. Pietri, and J. R. Weiss.

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