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THE PRODUCTION AND CERTIFICATION OF A PLUTONIUM EQUAL-ATOM REFERENCE MATERIAL - NBL CRM 128

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ABSTRACT

This report describes the design, production, and certification of the New Brunswick Laboratory plutonium equal-atom certified reference material (CRM), NBL CRM 128. The primary use of this CRM is for the determination of bias corrections encountered in the operation of a mass spectrometer. This reference material is available to the U.S. Department of Energy contractor-operated and government-operated laboratories, as well as to the international nuclear safeguards community. The absolute, or unbiased, certified value for the CRM's Pu-242/Pu-239 ratio is 1.00063 ± 0.00026 (95% confidence interval) as of October 1, 1984. This value was obtained through the quantitative blending of high-purity, chemically and isotopically characterized separated isotopes, as well as through intercomparisons of CRM samples with calibration mixtures using thermal ionization mass spectrometry.

PREFACE

Analytical tools are necessary to the plutonium production industry and to the U.S. Government in order to quantify inventories for safeguards and criticality control purposes. These tools include the instrumentation and techniques necessary to perform measurements on plutonium, as well as the reference materials needed to calibrate and validate the instruments and techniques. Reference materials also serve as controls for monitoring the reliability of a measurement system in order to assure that accurate results are maintained. These results are important to nuclear safeguards personnel since safeguards measurements data are almost exclusively derived from chemical and physical measurements. The role of reference materials in nuclear materials accountability is also emphasized by the U.S. Department of Energy (DOE) Order 5633.3 which requires that its contractor facilities which produce and handle plutonium establish measurement control programs that are "traceable to the national measurement base."

In 1972, the Atomic Energy Commission Divisions of Nuclear Materials Security and the Directorate of Regulatory Standards participated in the formation of the Planning Committee on Nuclear Calibration and Test Reference Materials. The primary task of the Committee was to define and evaluate reference materials needs for U.S. safeguards. The need for plutonium isotopic reference materials certified on an absolute basis was identified. In 1980, the DOE Office of Safeguards and Security assigned the highest priority status of need to the production of these reference materials for the U.S. and international nuclear safeguards community.

Over the next few years, reappraisals and rescoping of safeguards programs within the DOE resulted in the responsibility for these reference materials being placed within the functional activities of the New Brunswick Laboratory (NBL). The reference material activity described in this report, the production and certification of NBL CRM 128, was originally initiated by the National Bureau of Standards (NBS) of the U.S. Department of Commerce then transferred to NBL in 1983. At this time, NBL was given full technical and administrative responsibility for its completion.

I. INTRODUCTION

NBL CRM 128, Plutonium Isotopic Standard, was prepared by the quantitative mixing of nearly chemically and isotopically pure Pu-239 and Pu-242 solutions to yield the equal-atom isotopic mixture. A provisional (interim) certification of the CRM was provided based upon mass spectrometric data obtained relative to uranium. Absolute mass spectrometric certification measurements were subsequently performed using calibration mixtures with accurately known isotope ratios prepared from separated isotopes. The final experimental design relied almost entirely on the precision capabilities of the chemistry and instrumentation used in this effort. Mass spectrometer bias corrections determined from the isotopic analysis of these mixtures were applied to the equal-atom standard to yield an absolute value for its Pu-239/Pu-242 ratio. Therefore, the mass spectrometric analyses of the CRM and calibration mixtures provided the means of converting highly precise relative ratio values to highly accurate absolute ratio values. These mass spectrometric values along with mass and assay values were used to establish the certified value.

This report addresses activities beginning with the production and continuing through the certification of NBL CRM 128 on an absolute basis. These activities included the evaluation and, where necessary, the development of chemical and mass spectrometric procedures, as well as the implementation of these procedures to complete the production and certification of the CRM. Many techniques applicable to the purification and analysis of typical plutonium-bearing materials were used. The maximum capabilities of each method were exploited using high-purity chemicals and isotopic materials for the preparation of the CRM. As necessary, new methods were developed if existing ones were inadequate to achieve desired precisions. Throughout the course of this project, many investigations were conducted to assure the adequacy and sufficiency of these methods and achievement of desired results.

The final uncertainty assigned to the certified value of the CRM encompasses all significant errors generated in the elemental and isotopic values of the separated isotopes and in the preparation and isotopic analyses of the calibration mixtures. These errors were kept as small as possible. The certified value thus established for the CRM is accurate and precise to a very high degree.

It should be noted that all isotopic data presented in this report are in the form of the Pu-242/Pu-239 ratio, as actually measured during the certification effort. However, the certified ratio value is expressed as the reciprocal (Pu-239/Pu-242) of the measured values.

II. TECHNICAL APPROACH

The procedure for the determination of an absolute isotope ratio based upon mass spectrometry for plutonium leading to the certification of NBL CRM 128 is similar to the design of the mass spectrometric atomic weight method developed by NBS. This method has been previously described in the literature[1,2,3,4] and is shown in Figure 1.

Since highly precise and accurate atomic weights rely on precision wet chemistry and mass spectrometry to determine absolute atom ratios, this basic design provided a good model for the certification effort. To incorporate the production of the synthetic CRM and to include both the provisional and absolute certification efforts, a more detailed scheme was generated. The specific tasks of these production and certification efforts are described as follows.

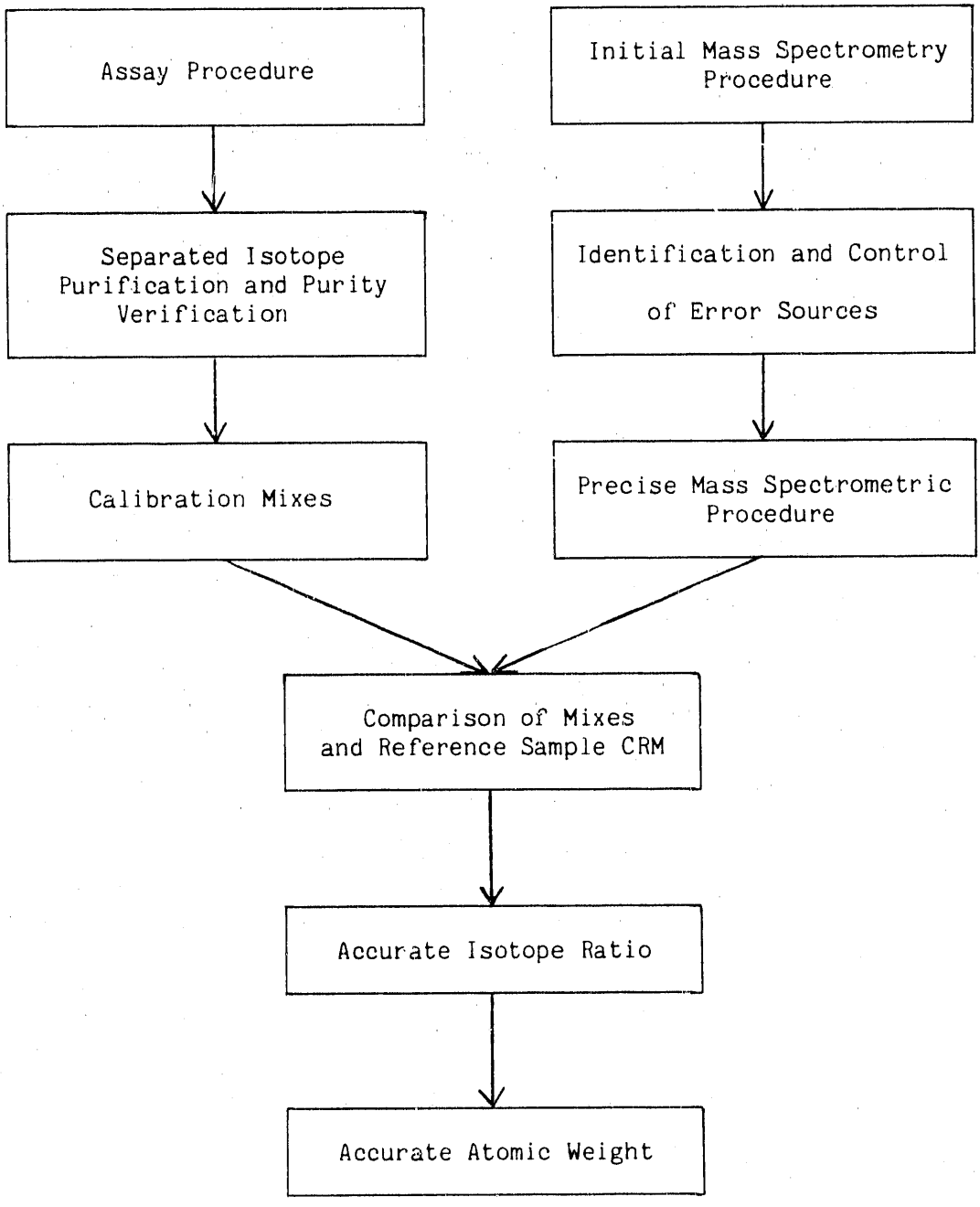

Figure 1. Mass Spectrometric Atomic Weight Method

A. Development of Purification and Assay Methodology

1. Development of purification procedure to remove, or reduce to tolerable levels, all species potentially interfering with the assay or mass spectrometric analysis.
2. Experimental validation of the purification procedure by impurities doping and verifying effects by appropriate analytical measurements.
3. Development of high precision plutonium assay method.
4. Statistical validation of assay method.

B. Development of High Precision/High Sensitivity Mass Spectrometric Procedure

1. Development of a highly precise and highly sensitive mass spectrometric method for the analysis of the separated isotopes as well as blended isotopic materials.
2. Assessment of possible sources of interference and error in plutonium isotopic measurements.
3. Statistical validation of the precision of the isotopic ratio measurements.

C. Preparation of the Reference Material

1. Acquisition of Pu-239 and Pu-242 isotopic materials.
2. Purification of each separated isotope.
3. Blending of aliquots of each separated isotope by weight and subsequent equilibration to yield a reference material with a Pu-242/Pu-239 ratio near unity.
4. Calculation of Pu-242/Pu-239 ratio using weight aliquotting and assay data (gravimetric method).
5. Preparation of individual units (actual reference material).
6. Packaging and final preparation for distribution.

D. Provisional Certification of the Reference Material

1. Coulometric assay of each subsample of the separated isotopes used to prepare the reference material.
2. Mass spectrometric measurement of the reference material relative to NBS Standard Reference Material (SRM) 947, Plutonium Isotopic Standard.
3. Calculation of the Pu-242/Pu-239 ratio of the reference material, mass spectrometrically bias corrected to the plutonium isotopic SRM.
4. Statistical analysis of all data and recommendation for provisional certification.

E. Certification of the Reference Material on an Absolute Basis Using Mass Spectrometry

1. Blending of weight aliquots of purified separated isotope solutions to obtain calibration mixtures of known isotopic abundance.
2. Sampling and assay of each separated isotope aliquot to determine the plutonium assay and isotopic composition.
3. Calculation of exact isotopic abundance of each calibration mixture using available assay and isotopic data.
4. Mass spectrometric comparison of the calibration mixtures and the reference material.
5. Calculation of the absolute isotopic abundance, statistical analysis, and recommendation for a certified value.

These tasks were not necessarily performed in the order in which they appear here, since many activities were performed simultaneously by different personnel utilizing different processes and instrumentation. The results obtained, reflected in the certified values (provisional and absolute) and associated uncertainties for the CRM, incorporate the use of the best procedures and methods derived from these activities and their findings.

By assigning a provisional certified value to the new CRM relative to an existing plutonium isotopic standard (NBS SRM 947), NBL was able to make the CRM available to the nuclear community in a shorter period of time. NBS SRM 947 was considered the most appropriate reference since the calibration would serve to relate the new CRM's value to other plutonium isotopic standards for the interim, until an absolute certification could be provided.

All assay, purification, and provisional certification measurements were performed at NBL, with the exception of impurity analyses which were done at Oak Ridge National Laboratory (ORNL). Absolute certification measurements were made at NBL; verification mass spectrometric measurements were made by Argonne National Laboratory (ANL). Each laboratory used the same mass spectrometric methods in the analysis of the CRM and calibration solutions. NBL analyzed the materials using Faraday cup detection. ANL analyzed each material using Faraday cup detection as well. However, ANL also chose to first mix its samples with a double, or internal, Pu-240/Pu-244 spike to enhance precision and to reduce run-to-run variations through the normalization of all data to the double spike ratio. The variations in the NBL and ANL methods of analysis provided useful information concerning comparisons of accuracy and precision of the specific methods and results.

The selection of procedures used to perform the different tasks necessary in this project was based upon predetermined goals for achieving the desired accuracies. Since a predominance of the work was based upon the generation of precise relative values of the Pu-239 and Pu-242 isotopes, reproducible procedures were highly desirable. This meant that somewhat biased values could be tolerated in the purification and coulometric assay of these plutonium materials. It is important to note this because only those biases which were determined to have an influence on the accuracy of the certification measurements were quantified.

The existence of mass spectrometric bias due to preferential depletion of the lighter isotopes being vaporized has long been studied. This effect itself and the resulting bias are "correctible" by the analysis of calibration mixtures of known isotopic contents in conjunction with the "unknown" reference material. The key consideration in reproducing this bias is not only the careful control of parameters such as sample quantity and burn temperature, but also taking data at the same point in time on the theoretical fractionation curve. This approach best approximates the bias and allows for precise corrections to be made.

Degassing the sample filaments to reduce or eliminate interferences, the strict adherence to the analytical procedures, and the maintenance of sufficient ion intensity to make circuitry noise levels in the mass spectrometer negligible and enhance sensitivity are additional factors that can augment precision. These and other parameters will be detailed later.

III. MEASUREMENTS PROCESS - INSTRUMENTATION AND SAMPLE PREPARATION

A. Instrumentation

The coulometer and mass spectrometer used in these experiments were vital in the completion of this reference material project. The quality of the analytical work produced was directly linked to the sophistication of these instruments and to their behavior during the measurement process.

Although more than one mass spectrometer was used in the project, this report will describe in detail only the instrument used by NBL for the provisional and absolute isotopic measurements work. Brief mention will be made in regard to the other mass spectrometer, used by ANL, which provided verification measurement information as described later in this report (Section X.D.).

B. Mass Spectrometry for Isotopic Analyses

1. Thermal Ionization Mass Spectrometer

The NBL mass spectrometer is an instrument of NBS design. It is a single-focusing solid sample thermal ionization instrument with a 30-cm radius of curvature, 90° analyzer tube and magnet sector. Detailed descriptions of this instrument have been made available by NBS.[5] The instrument is shown in Figure 2.

The mass spectrometer is equipped with a thin lens "Z"-focusing ion source developed by NBS in the mid-1960's to increase ion transmission (Figure 3). This increase in transmission permits attainment of ion signal intensities at low filament temperatures and with a correspondingly low rate of fractionation.

The collector is a deep-bucket Faraday cup equipped with a 50% transmission grid shadowing a series of suppression grids. The purpose of the suppression grid system is for the reduction of secondary particles which are generated, as well as for elimination of random bias created by the energy of the ions, magnitude of the ion current, and the degree of cleanliness of the collector.

The measuring circuit consists of two vibrating reed electrometers (Cary 401) operated as a master-slave combination. The slave unit is used to monitor that portion of the ion total current collected by the transmission grid. The grid signal provides a quick and reliable means of establishing uniform ion intensities which are necessary in high precision work. Also, sudden changes in the grid signal indicate problems with either the sample or instrument function. The master unit is used to measure the ion currents collected at the Faraday cup. The ion currents

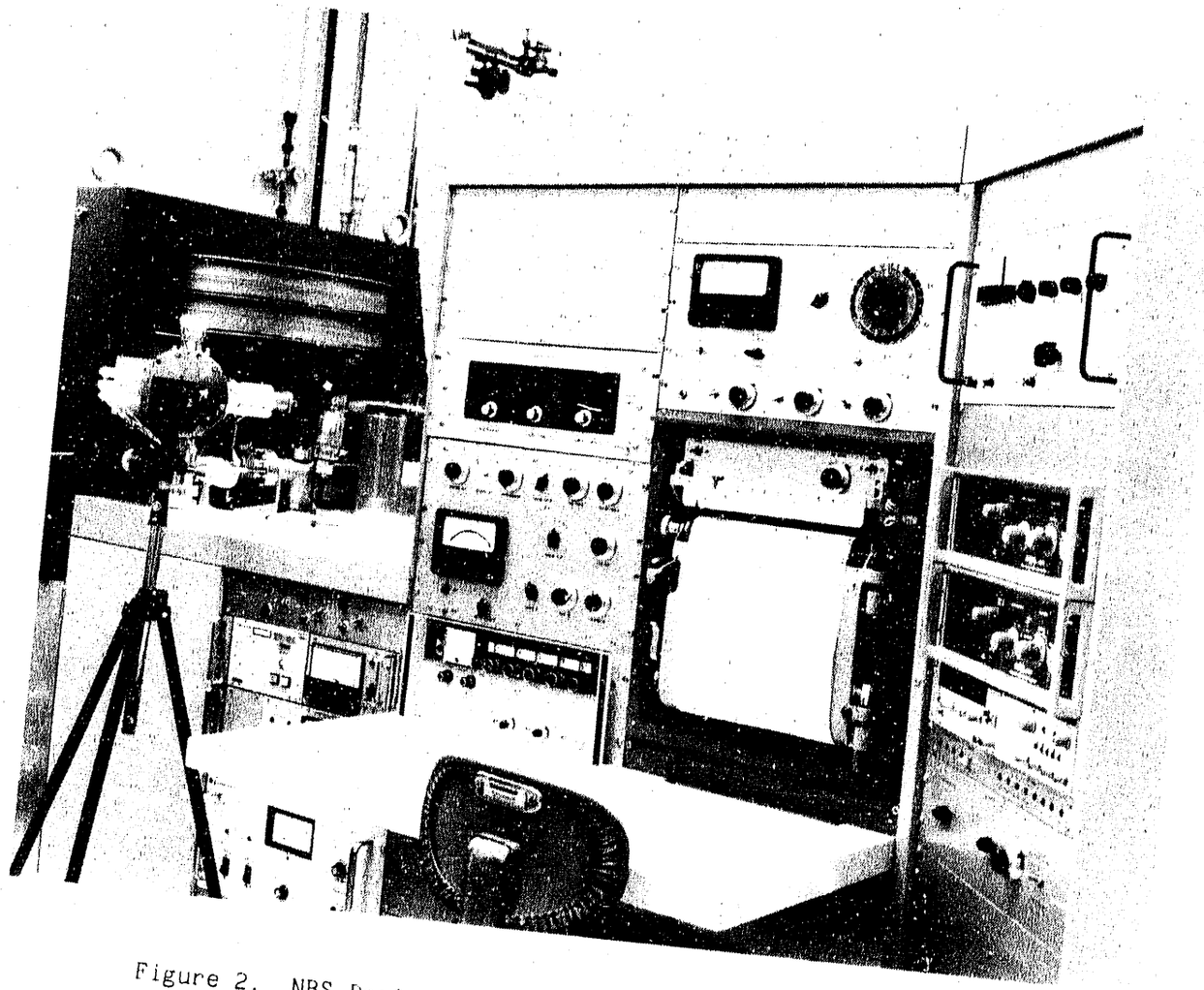

Figure 2. NBS-Design 30-cm Radius of Curvature, 90° Magnetic Sector Solid Sample Mass Spectrometer

Figure 3. Thin Lens "Z"-focusing Ion Source

generated for each isotope are used to calculate isotope ratios. These ratios are then used to determine relative isotope abundance values. Due to the magnitude of the ion currents generated (10^{-11}A), input resistors of 10^{11} Ω are used by the two units.

Instrument operation and data collection are performed by a Hewlett-Packard (HP) 9826A Desktop Computer interfaced with the instrument. Analog ion-signal intensities from the master electrometer are digitized using an HP 5345 Digital Voltmeter and read by an HP 9826A. The HP 9826A also controls the FR-41 Gaussmeter/Controller equipped with a Hall probe which allows for quick and reliable peak switching and centering. A hard-copy printout of the data is made available using an HP 9866 Thermal Printer.

Additional features of the mass spectrometer are the ultra-high vacuum system, consisting of a 175 L/s turbomolecular pump mounted beneath the source housing for source pumping, and a 200 L/s ion pump on the analyzer tube. Additional pumping is achieved by filling a cold trap (located above the source housing) with liquid nitrogen.

An expanded scale circuit feature of the instrument was utilized in the isotopic measurements of the pure Pu-239 and Pu-242 isotopic starting materials. In the standard mode of operation (unexpanded scale), the chart recorder which graphically plots the level of the intensity measured by the master electrometer produces a recorder pen deflection equivalent to the degree of voltage saturation of the particular electrometer voltage scale. This deflection is "expanded" by placing the 1/10 increment of the deflection over the entire range of the recorder scale. This enhances the signal by an order of magnitude

and allows for more precise peak centering to be performed where peak heights are small. The benefit is a more precise and accurate "setting up" of minor peaks which translates to better precision on the particular measurement. As can be seen by the data for these pure isotope materials, precisions for <100 ppm isotopic abundances were achieved within ten ppm, or one one-thousandth of a percent.

2. Sample Preparation

Studies performed by NBS in the 1960's indicated that significant systematic differences arise in measured isotope ratio values due to variations in the acidity of solutions for analysis in a mass spectrometer. These studies also found that neutral solutions (non-acidic) were harder to analyze than acidic solutions. Furthermore, plutonium solutions which are neutral can cause the plutonium to polymerize and become nonreactive. These two observations have established the need to maintain the plutonium in an acidic medium during storage and for sample mounting.

A solution prepared with 1 $\underline{N}$ HNO_3 seemed to be ideal for mass spectrometric purposes and was used to prepare all samples. At this acidity no polymerization was observed and the resulting dried oxide material on the filament was easy to vaporize and ionize, yielding adequate ion intensity without excessive changes in the rate of fractionation. Also, the solution had sufficient surface tension to dry as a small droplet on the filament without spreading over the length of the filament and causing non-uniformity in fractionation behavior.

3. Sample Mounting

Since thermal ionization mass spectrometry (TIMS) is an ion production and measurement process, much consideration must be given to the ion production aspects of the system. The relative number of ions formed from the volatilized neutral atom vapor depends primarily on the ionization potential of the sample atoms, the temperature at which the filament is operated, and the work function of the filament material. Generally, the higher the temperature of the filament, the greater the percentage of ions produced. Since the ionization potential is fixed for an atom or compound of a particular element, additional ionization efficiencies can only be obtained by the increase of the work function of the filament material. Further, plutonium requires relatively high temperatures for sufficient ionization, so the filament material must be a refractory metal with a high work function surface.

There are several techniques for increasing the ionization efficiency while controlling the evaporation rate. Multiple filament arrangements in which the sample is evaporated from one filament and ionized on another have been demonstrated to be an effective way to achieve these goals.

Rhenium was used as the filament material in all experiments performed in this project. Rhenium is an excellent material for this purpose due to its high work function (25 eV) and because it is quite flexible and can be easily spot-welded to support posts. Also, it has a low vapor pressure at the usual temperatures of operation (1000-2200°C). Poly-crystalline rhenium is commercially available at reasonable prices, and can be obtained as a highly pure (99.99+%) metal prepared by electron beam zone-refining.

The plutonium samples analyzed in this project were loaded on 0.030-mm X 0.76-mm rhenium filaments. The rhenium, although highly pure, was degassed immediately prior to use under a vacuum of $6.7 * 10^{-5}$ Pa ($5 * 10^{-7}$ torr) in a potential field. This additional clean-up depleted the filament of interstitial oxygen and degraded the levels of alkali and organic materials, which helped reduce pressure levels inside the ionization source during sample analysis. A few microliters of sample solution containing microgram per milliliter quantities of plutonium were then loaded on each of two filaments to be mounted in the multiple filament configuration. Exact sample sizes were evaluated independently to determine preferential sample loads to be used during the certification measurement stages.

The sample filaments were placed into a filament block and alignment of the two sample filaments with respect to the central or ionizing filament made visually. The ionizing filament was centered in the block with the aid of a support stand using tweezers and the sample filaments were moved apart approximately 0.5 mm from the edges of the ionizing filament. The assembly was then inserted into the mass spectrometer source and placed under vacuum. Photographs of the filament block and source are shown in Figures 4 and 5, respectively.

C. Coulometry for Elemental Analyses

1. Controlled-Potential Coulometer For Elemental Assay

Plutonium wet chemical assay measurements performed in support of the CRM certification utilized the NBL controlled-potential coulometric (CPC) analysis.[6] The

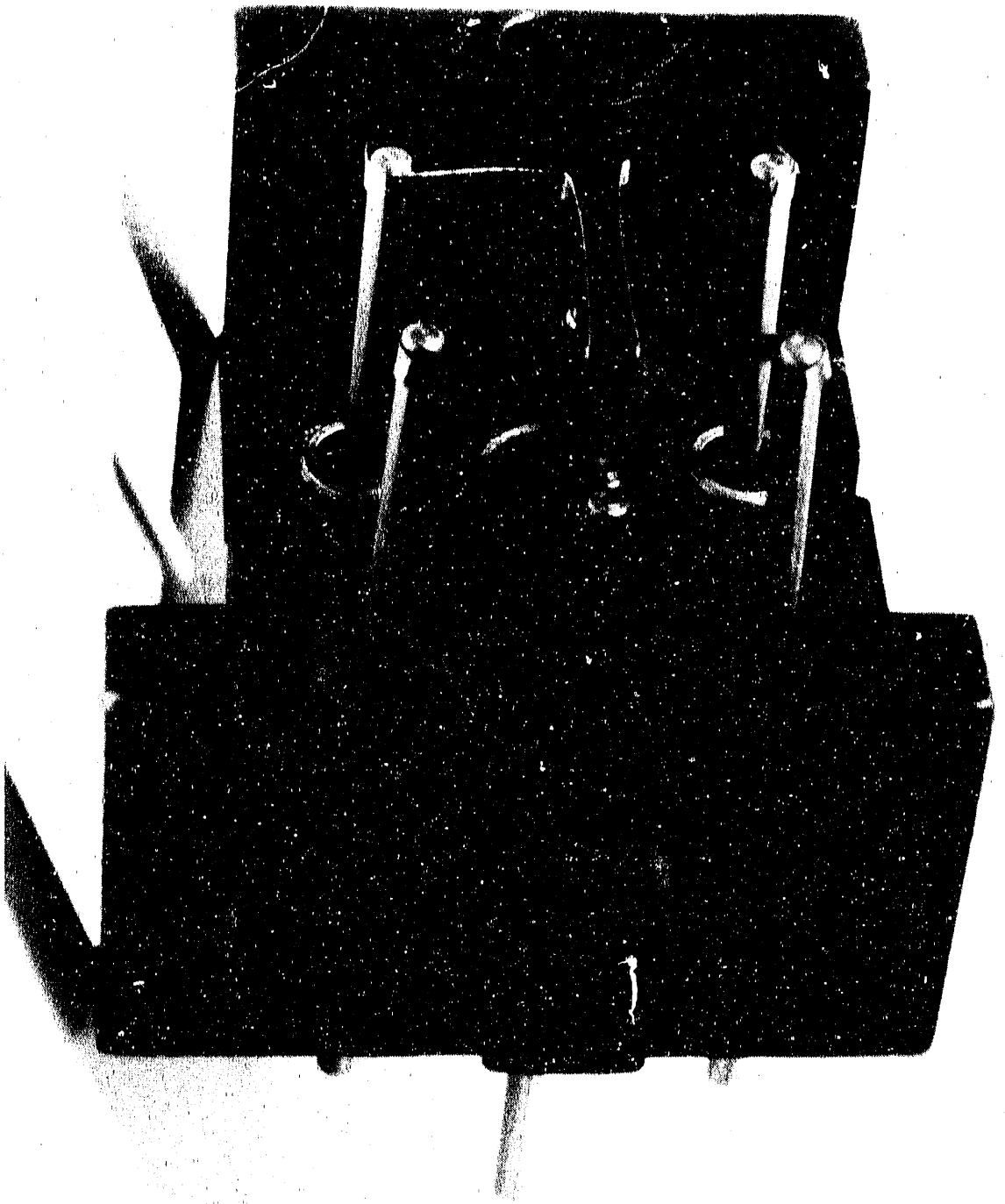

Figure 4. Filament Block Assembly

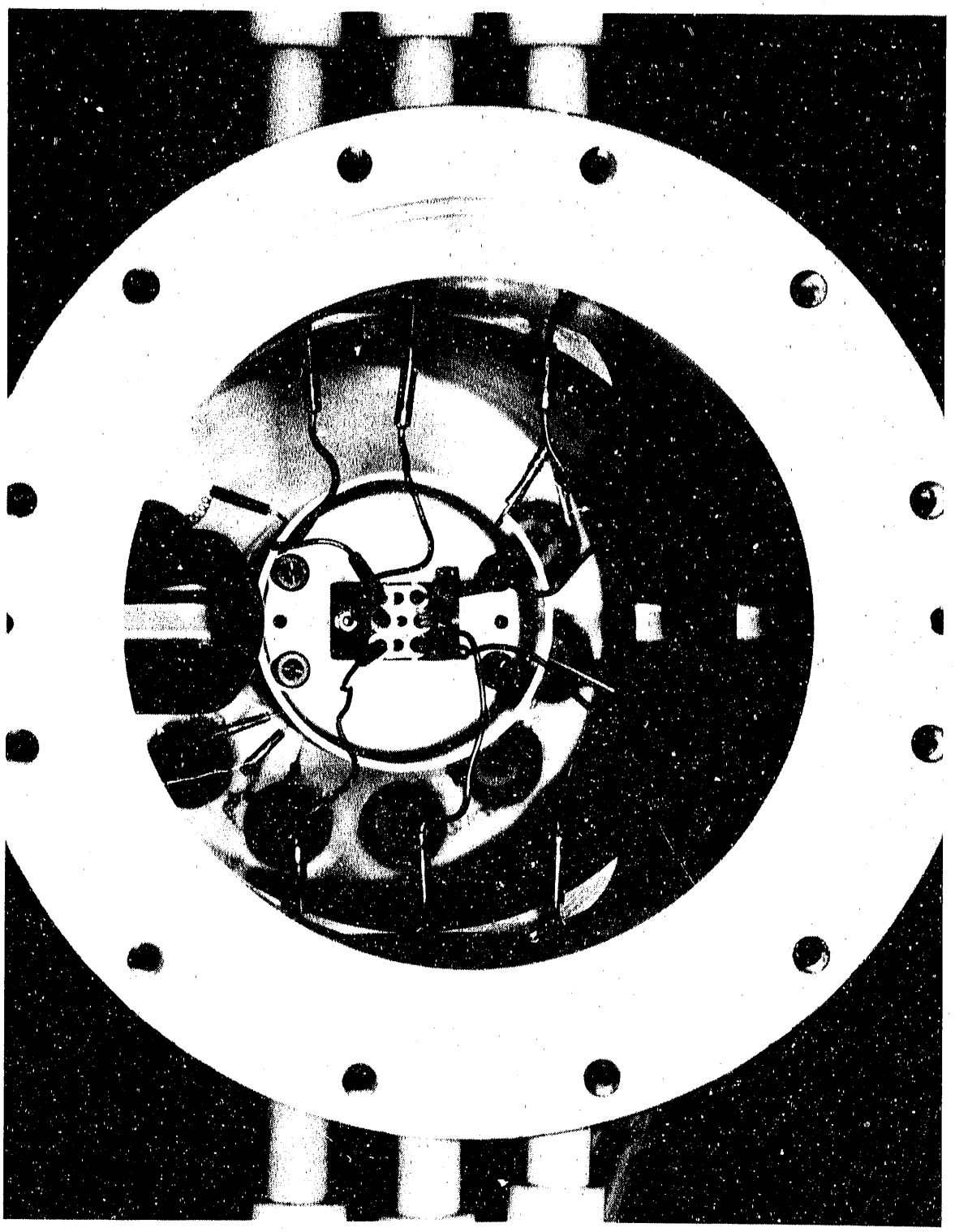

Figure 5. Mass Spectrometer Ion Source Housing

method consists of reduction of Pu(IV) and subsequent oxidation from Pu(III) to Pu(IV) in a supporting electrolyte. The quantity of charge necessary to electrolyze the Pu(III) to Pu(IV) is integrated throughout the electrolysis period. The total coulombs of electrical charge, in conjunction with a calibration factor in coulombs of electricity per mole of plutonium and the atomic weight of the plutonium are used to calculate total grams of plutonium in the sample. The calibration factor is determined on a continuous basis using a potentiostat and precision resistors and is traceable to the Faraday Constant. Studies performed using NBS SRM 949e Plutonium Metal Assay Standard have demonstrated that the NBL CPC method is capable of a mean recovery range of 99.97-100.01% with a RSD range of 0.02-0.07%.[6]

NBL used the MT Electronics Co. Model 3 Coulometer, which is automated through the use of an HP 9825A microcomputer. The coulometer is shown in Figure 6. Samples were changed manually, using cut-down 50-mL glass Griffin beakers as reusable coulometry cells. The coulometry cell head assembly is detailed in Figure 7. Optimum sample size used was 5-10 mg of total plutonium. The sample was dried to the sulfate form prior to analysis to stabilize the Pu(IV) oxidation state and to remove volatile anionic species, such as Cl^- and F^-, which are added during dissolution of plutonium metal and oxide samples.

Because there are also non-volatile elements, most notably iron and neptunium, which are electroactive in the region of the Pu(III) - Pu(IV) couple and thus constitute an interference in the analysis, the bulk of interfering elements was removed from the CRM samples prior to coulometric analysis utilizing the macrocolumn anion-exchange procedure detailed in Section V.B. A routine

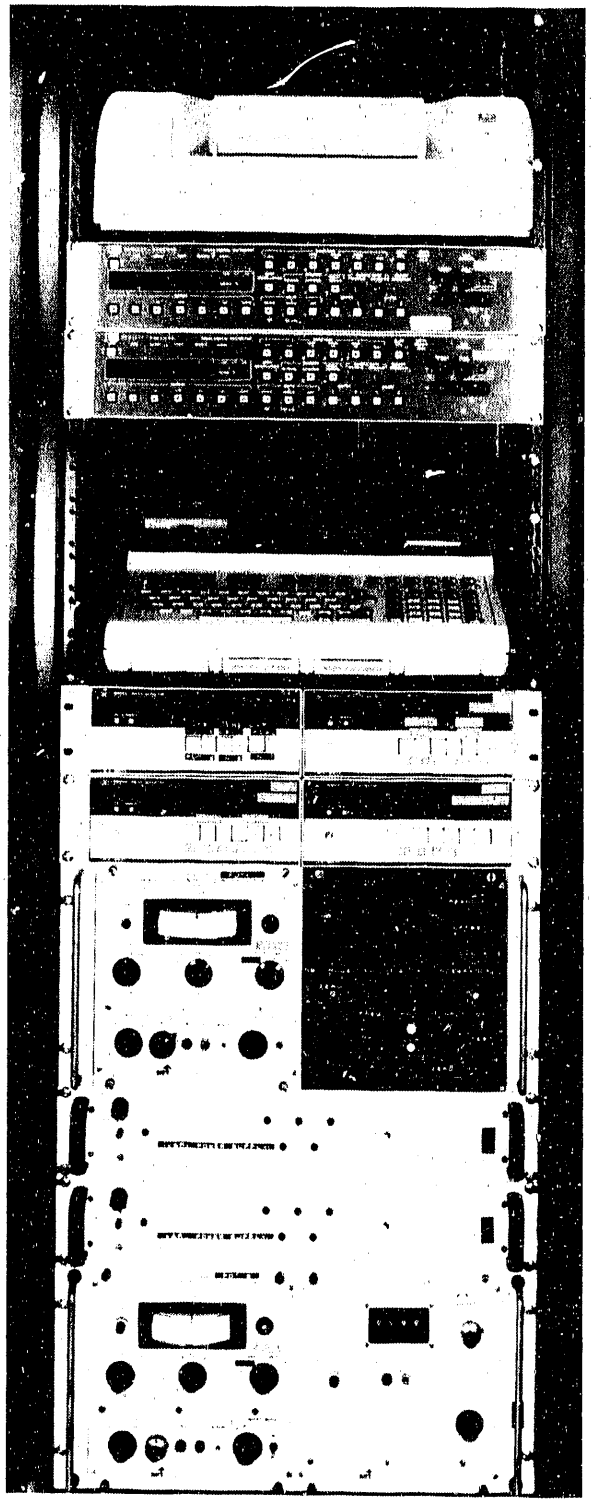

Figure 6. Controlled-Potential Coulometer

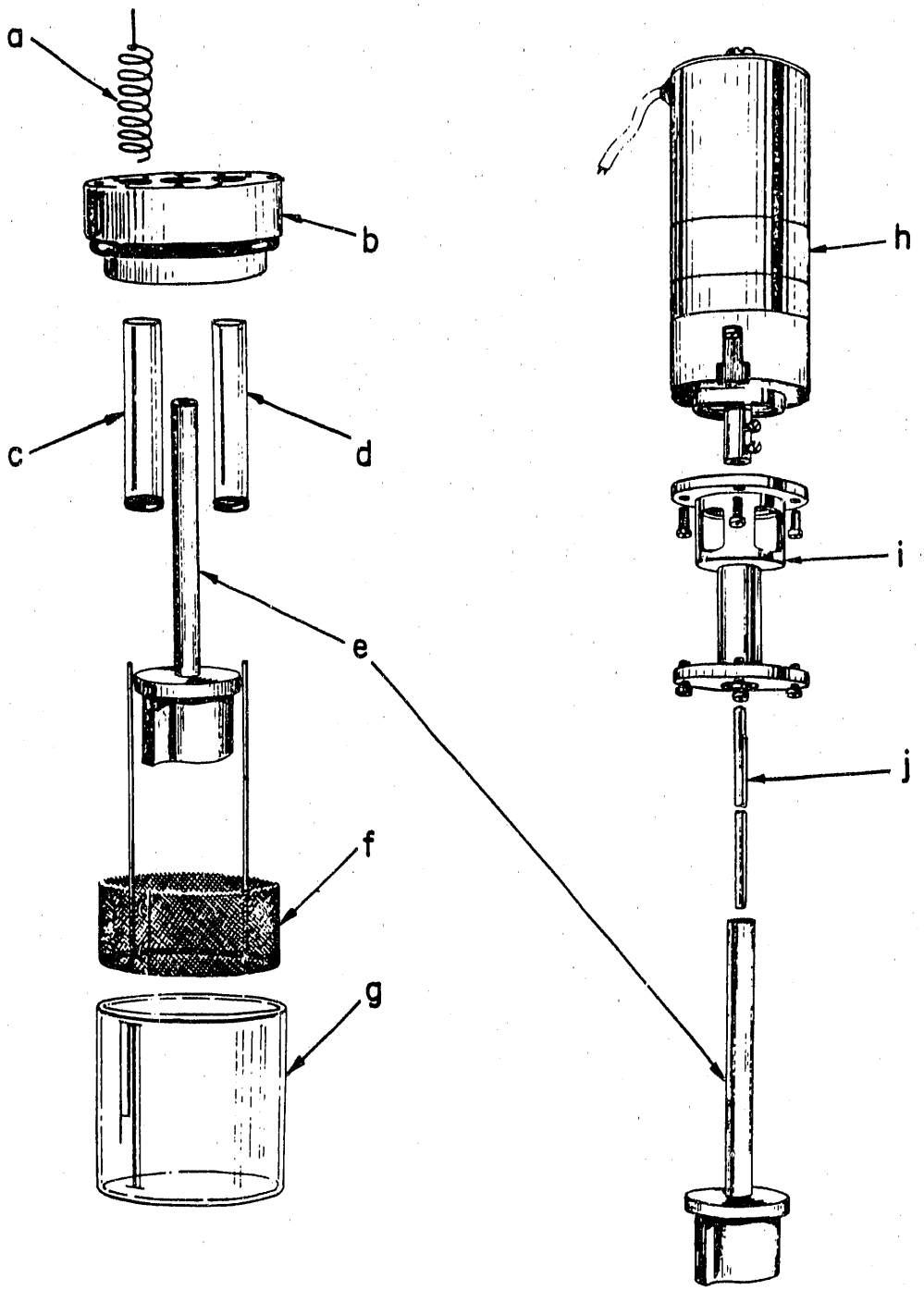

Figure 7. Coulometry Cell Head Assembly

(a) platinum counter electrode, (b) coulometer cell head, (c) counter electrode salt bridge tube, (d) reference electrode salt bridge tube, (e) NBL-designed S-shaped stirrer, (f) working electrode, (g) coulometer cell, (h) stirrer motor, (i) stirrer motor pedestal and bearing housing, and (j) stirrer drive shaft.

analysis required approximately 45 minutes to complete both the blank electrolyte and sample measurements. As each electrolysis neared completion, the potential was adjusted until current flow in the cell was zero. Calculations derived from the Nernst equation were then employed to correct for the fraction of plutonium which had not been electrolyzed (<0.05% of the total sample).

2. Sample Preparation and Analysis

Sample preparation and analysis relating to controlled-potential coulometry are summarized here. Eighteen to twenty mL of 0.9 N HNO_3 and three drops of saturated NH_2SO_3H (sulfamic acid) were placed in a clean coulometry cell which was then connected to the cell head of the cell assembly. The electrolyte solution was reduced and then oxidized to predetermined potentials. The electrolyte was then transferred to another coulometry cell containing the dried plutonium sample and that cell connected to the cell head. A similar reduction-oxidation was performed as previously described for the blank. The working electrode versus reference electrode potentials, integrator output, and electrolysis times were recorded. Mathematical calculations performed using these factors determined plutonium content in the sample.

Details of the sample preparation, coulometric determination of plutonium, and operating procedures for the coulometer have been documented.[6] These procedures take into account accurate corrections for background current, the fraction of plutonium not electrolyzed, and systematic errors which arise from electrical integrations.

IV. APPARATUS

A. Syringes and Bottles for Solution Aliquotting

Preparation of all plutonium solutions used in this project was accomplished through weight dilution and aliquotting. The use of these techniques, which are based on precise and accurate mass measurements, served to minimize the contribution of weighing and sampling errors to the overall uncertainty in the CRM's Pu-242/Pu-239 ratio.

The specific weight aliquotting techniques adopted by NBL had been originally developed by NBS and involved use of a plastic syringe and bottle assembly to contain, withdraw, and weigh the sample. Figure 8 shows the apparatus used at NBL for sampling. Each plutonium sample was placed in an acid-leached TFE-fluorocarbon bottle, which helped to minimize both impurity contaminations and evaporative losses of sample material during storage. The sample was diluted by weight with 8 $\underline{N}$ HNO_3 and thoroughly mixed. The Teflon screw-cap was then discarded and replaced with a hollow plastic stopper. This stopper had a hole punched through the bottom and small diameter (~3 mm) TFE-fluorocarbon tubing threaded through the hole. (Thus the tubing provided access to an otherwise sealed bottle of solution.) A polychlorotrifluoroethylene hub was then fitted onto the outer end of the tubing to provide a leak-tight seal around a disposable plastic syringe. This syringe of appropriate size, usually 5-, 10-, or 20-mL, was attached to the hub and solution brought into the syringe by withdrawing the plunger. The tip of the syringe was disengaged from the seal, wiped, capped and the entire syringe assembly weighed. The sample aliquot could then be expelled into a beaker or another TFE-fluorocarbon bottle, the syringe immediately reweighed and the aliquot weight calculated by difference. With this

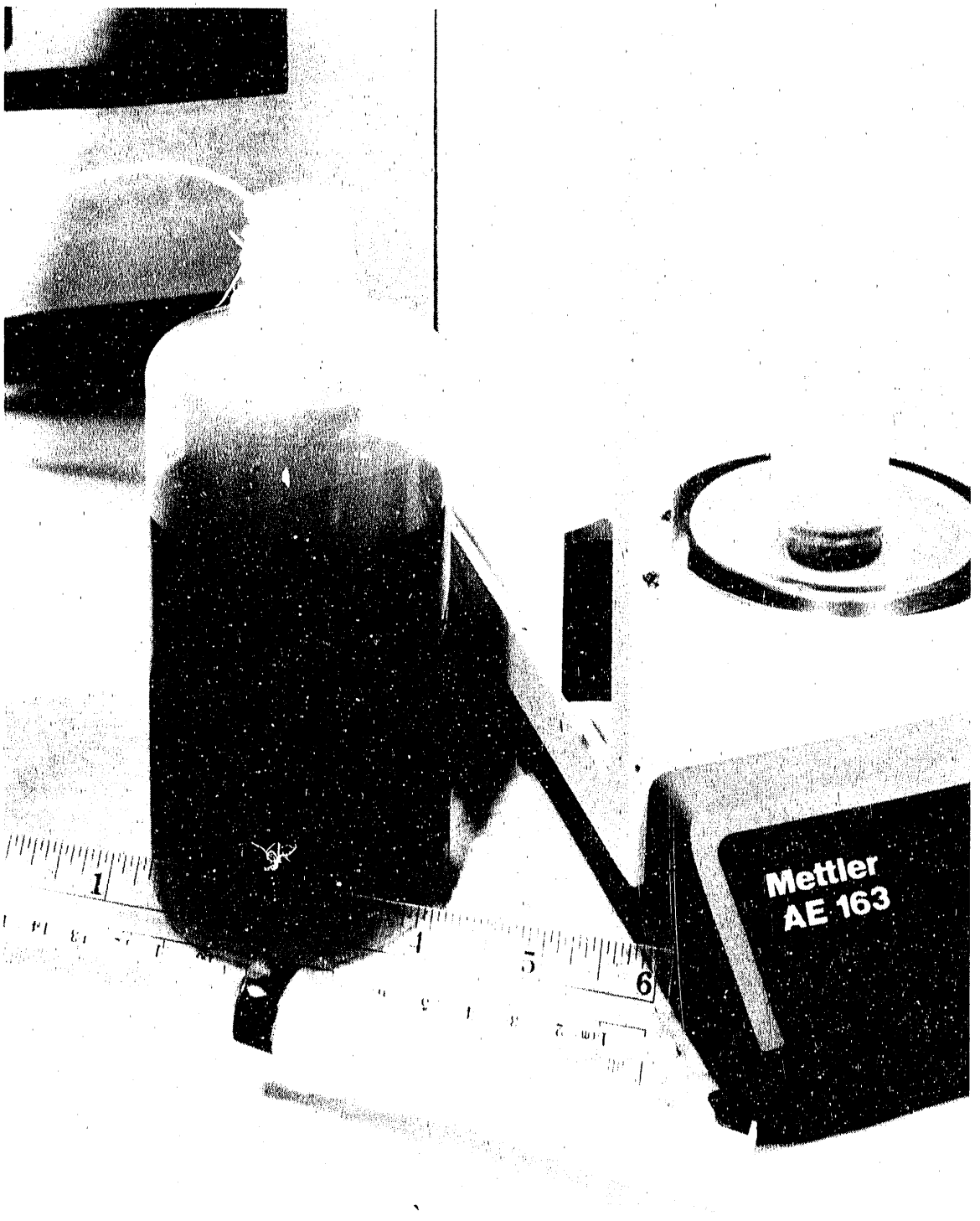

Figure 8. NBS Syringe and Bottle Assembly for Solution Aliquotting

technique, solution aliquots could be taken without ever exposing the solution to potentially contaminating or evaporative effects of the glovebox.

As expected, static charge occasionally built up on the TFE-fluorocarbon bottles and plastic syringes. However, it could be dissipated by wiping bottle or syringe surfaces with a damp, lint-free cloth. This approach was sufficient to eliminate drift due to static charge on nearly every weighing. Nonetheless, when a weight drifted by more than 0.05 mg (0.005% or less), the sample was discarded or the syringe reweighed.

It should be noted that the master solution of the CRM was subsplit into individual units for distribution using an assembly the same as that just described, except that a Drummond repeating pipette was substituted for the plastic syringe. The use of the Drummond pipette provided for rapid, reproducible (±3%) dispensing of the master solution. Each aliquot was weighed by difference into a 30-mL TFE-fluorocarbon bottle, for calculation of its nominal plutonium content. The apparatus used to aliquot the CRM is shown in Figure 9.

B. Electrochemical Cleaning Apparatus

NBL obtained approximately 5 g each of high-purity Pu-239 metal and Pu-242 oxide from ORNL for use in preparing the CRM. No cleaning of the Pu-242 oxide material was required. However, the metal arrived in the form of several heavily oxidized, wafer-thin pieces which required removal of the oxide coating prior to weighing and dissolution. When it was determined that NBL's routine mechanical abrasion technique would not work in this case due to the varied sizes and thicknesses of the metal pieces involved, a potassium carbonate-electrolytic cleaning technique was investigated as an alternative method for cleaning the metal.

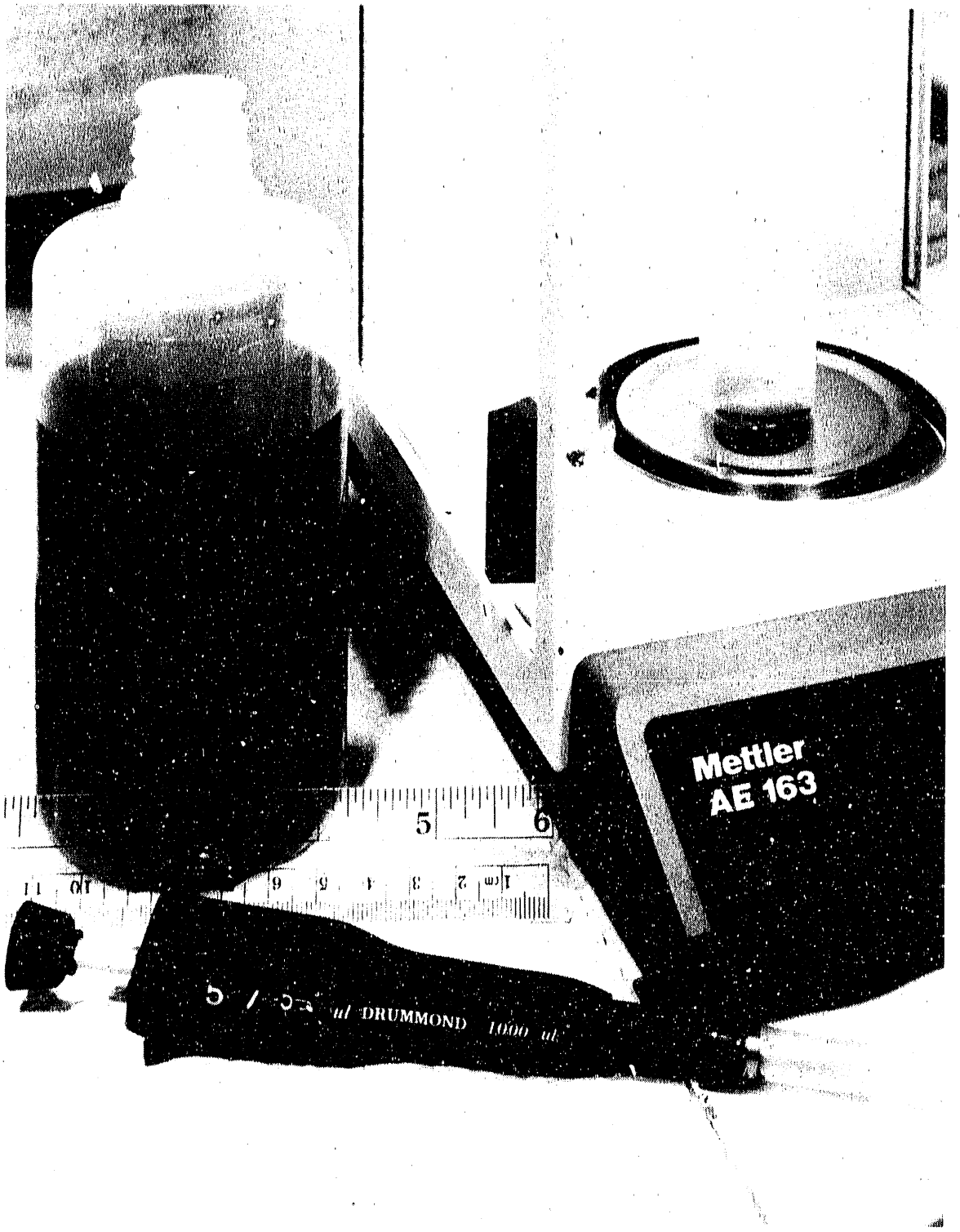

Figure 9. NBL CRM 128 Aliquotting Apparatus

The procedure can be found in the literature,[7,8] and is described as follows. The metal sample is placed in a 15-mL platinum crucible and 5-10 mL of 20% K_2CO_3 are added. A platinum wire cathode and the platinum crucible anode are then wired to a power supply (three 1.5-V dry cells, connected in series) and the platinum wire is touched to the surface of the plutonium metal. The reaction proceeds with the evolution of hydrogen gas and the formation of the green plutonium-carbonate complex. The cleaned metal is then rinsed with water, air-dried, and immediately weighed and dissolved. A photograph of the actual electrochemical cleaning apparatus is shown in Figure 10.

C. Balances For Weighing and Mass Measurements

The NBL CRM 128 calibration solutions and coulometry samples were weighed on a Mettler H51AR balance, certified accurate to ±0.02 mg. This balance is the most precise and accurate instrument available for this measurement in NBL's plutonium laboratory. Limitations of the H51AR balance capacity (160 g) and physical location precluded its use for all weight measurements associated with this project. Sample dilutions and blending of the NBL CRM 128 master solution were accomplished using a Mettler H315 balance, certified accurate to ±0.1 mg. Weights of the individual CRM units were measured on a Mettler AE163 top-loading balance which is accurate to ±0.2 mg and is equipped with a printer.

All NBL balances are serviced every six months, with a certification of balance accuracy issued relative to NBS Class M Weights. A set of Class M Weights is dedicated to the plutonium laboratory balances and these weights were used to check all balances prior to their use for the CRM measurements. The electrical calibration of the AE163 balance using an internal 100-g weight, was also checked using a Class

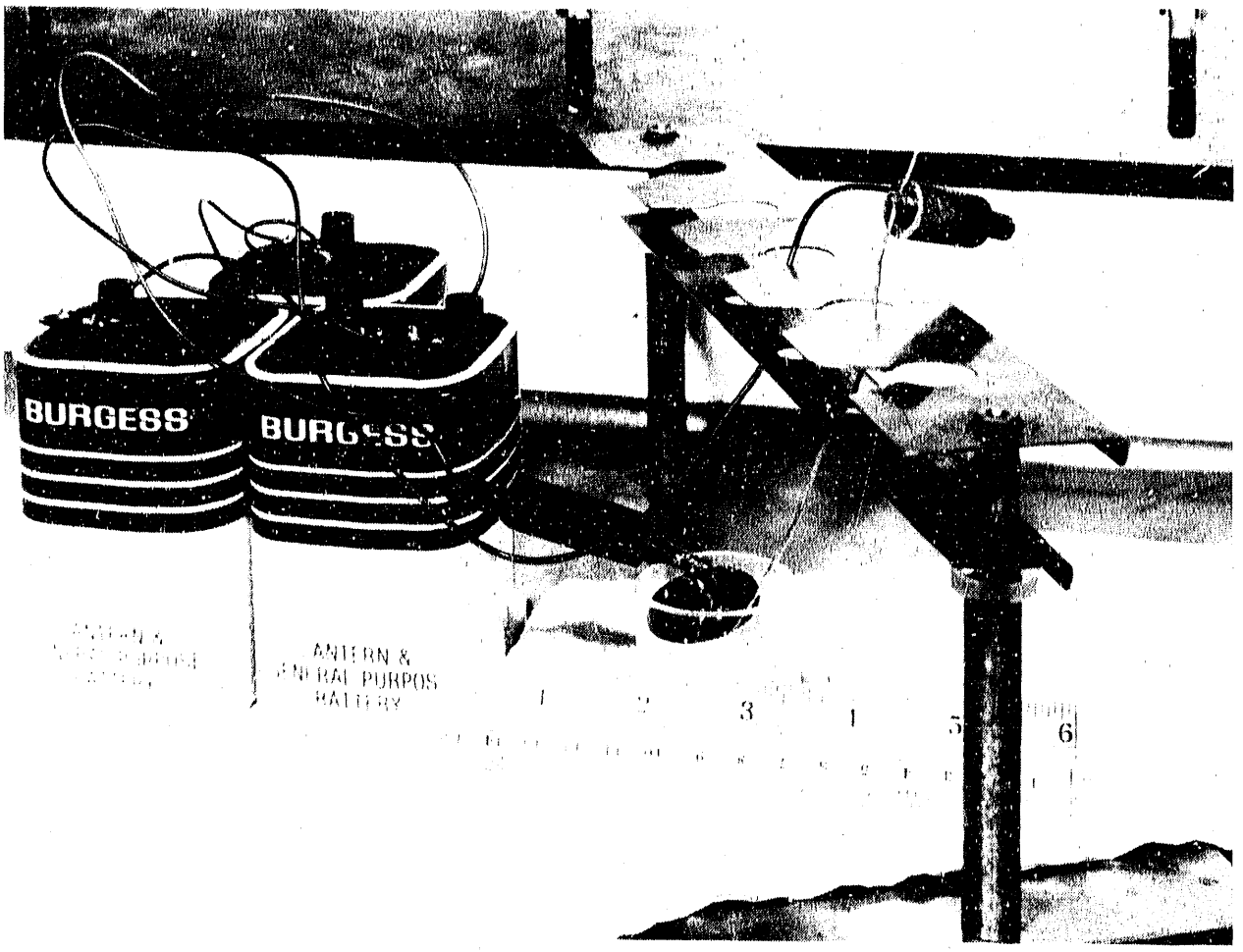

Figure 10. Electrochemical Cleaning Apparatus

M 100-g weight. Air bouyancy corrections were made for the master and calibration solutions aliquots; however, when calculating the plutonium isotopic ratios for each solution, the corrections effectively cancelled.

D. Microsyringe for Mass Spectrometric Sample Loading

Calibrated glass microsyringes were used to dispense sample solutions onto filaments for mass spectrometric analyses. This type of pipette was preferred over the disposable, glass-drawn pipettes which are made within the laboratory, due to the requirements for high accuracy and reproducibility in solution quantities. The disposable tip, made from non-wettable inert polytetrafluoroethylene (PTFE), was the only part of the instrument in contact with the liquid sample, so cross-contamination was not a problem. A microsyringe with a capacity of 5 mL, and graduations of 0.2 mL, was used and was specified by the manufacturer to have a repeatability of ±1%. Previous work, as well as work performed during the evaluation portion of this project (Section V.D.), indicated that this degree of repeatability would be adequate to meet the desired precision of this certification.

Figure 11 is a photograph of the microsyringe with a disposable tip (foreground). In the background is a sample filament assembly and support stand designed to hold one or two filament assemblies.

V. EVALUATION OF CHEMICAL AND MASS SPECTROMETRIC TECHNIQUES

A. Electrochemical Cleaning of Plutonium Metal

Before applying the method to the CRM starting material, the effectiveness of the electrochemical cleaning technique was evaluated by comparing assay results for electrolytically

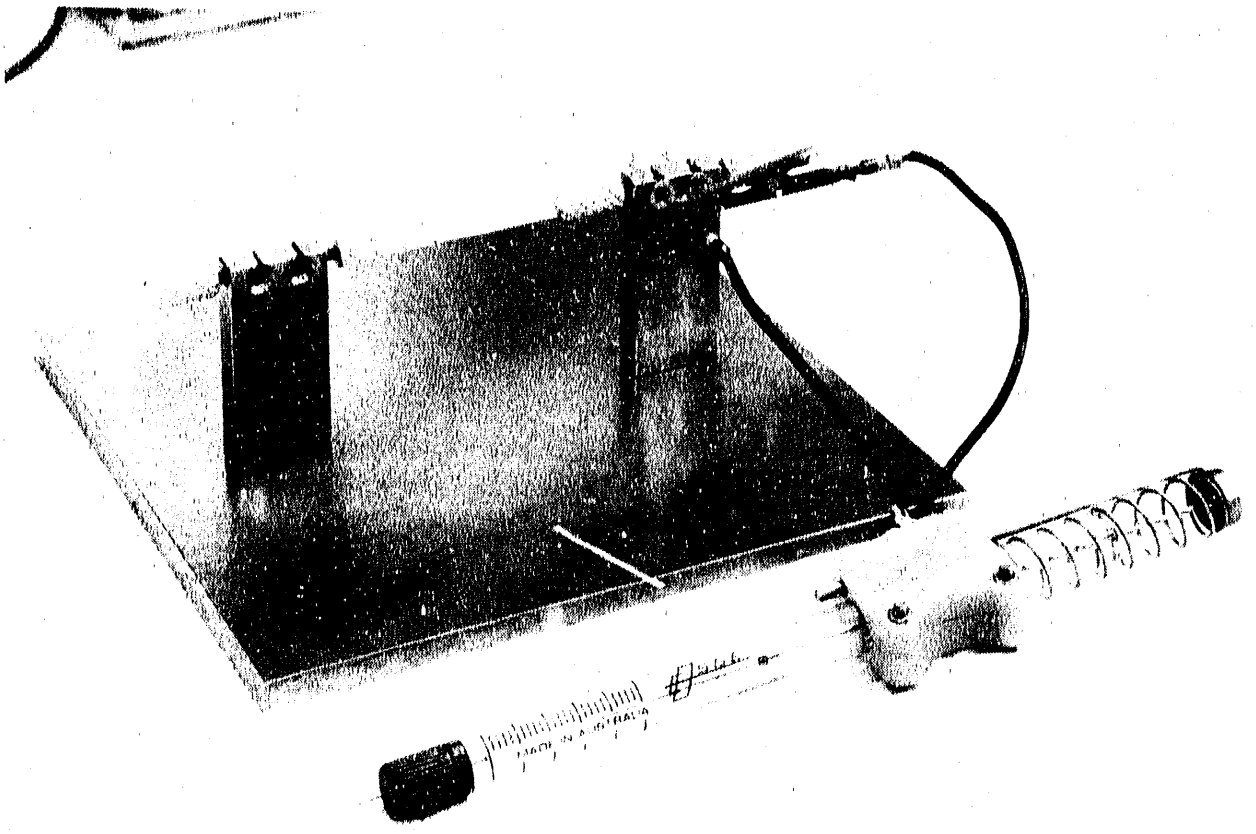

Figure 11. Microsyringe for Mass Spectrometric Sample Loading

cleaned metal samples to assay results for samples of the same metal cleaned by mechanical filing. Samples from the Rocky Flats Plutonium Metals Exchange Program were used in this study. The results obtained were compared to Exchange values which were established on an interlaboratory basis.

As shown in Table I, coulometric results obtained for samples of A81, B81, and C81 electrocleaned metals were all statistically identical to NBL's reported data obtained using the filing technique. Data for the electrochemical method exhibited an overall precision of less than 0.02% standard deviation. This was slightly better than the 0.03% standard deviation on NBL's reported Exchange data for these samples. Results for the B81 Metal agreed quite well with other coulometric data (Exchange-CPC) and with the Exchange average for all methods. The A81 and C81 metals agreed with other coulometric data, but were 0.10-0.15% low as compared to the Exchange average for all methods. The observed differences were contained within the error associated with the Exchange average for all methods. High levels of precision and accuracy, which

TABLE I

Evaluation of Electrochemical Cleaning of Plutonium Metal

Method	Metal A81		Metal B81		Metal C81	
	Assay(%)	%RSD	Assay(%)	%RSD	Assay(%)	%RSD
Electro-chemical	99.420	0.020	99.906	0.016	99.458[a]	0.010
					99.463[b]	0.007
Mechanical Filing	99.430	0.027	99.864	0.038	99.476	0.028
Exchange-CPC	99.438		99.896		99.374	
Exchange-All Methods	99.590		99.903		99.530	

[a]Analyst 1
[b]Analyst 2

NBL obtained on its quality control NBS SRM 949e and 949f Plutonium Metal Assay Standards, verified that the coulometric assay was operating within control limits during the elapsed time of this study. The degree of agreement achieved between data sets demonstrates that the electrochemical procedure is effective in cleaning plutonium metal samples.

The electrochemical cleaning method also holds several advantages over the mechanical abrasion methods. Of chief interest in the CRM work is the decreased contamination of the metal sample with iron and other trace elements from use of a triangular file. There is also the reduced risk of fire and radioactive contamination. Plutonium oxide, as it is removed from the metal surface, forms a soluble plutonium-carbonate complex with the electrolyte. This eliminates handling of the pyrophoric metal filings and reduces the associated fire hazard. The potential for releasing radioactive contamination is also decreased when using the electrochemical method. Furthermore, the geometrical shape of the metal sample is no longer a factor, as the technique is easily adaptable to various sample shapes and sizes. Lastly, the equipment needed for the electrochemical technique is simple, inexpensive, and easily adaptable to glovebox work. In summary, the electrochemical cleaning technique has been demonstrated as an effective alternative method to mechanical filing for the removal of surface oxide from plutonium metal in a variety of shapes and thicknesses and was successfully used to clean the high-purity Pu-239 metal used in preparing the CRM.

B. Bulk Ion-Exchange Study

NBL traditionally employs an anion-exchange purification of plutonium samples to remove interfering elements, such as iron, before coulometric analysis. This purification consists of a quantitative ion exchange of each individual sample aliquot

immediately prior to the assay measurement. Quality control standards are ion exchanged and assayed concurrently with each batch of samples to track the accuracy of the analysis. In this way, errors which do occur are attributed to the analysis as a whole and not to either individual step. However, as part of the attempt to achieve a high-precision coulometric analysis for plutonium for this CRM project, the ion-exchange purification was separated from the coulometric analysis, so that any ion-exchange-generated error would not effect the overall precision of the assay. This was accomplished by performing a bulk ion exchange on each of the Pu-239 and Pu-242 isotope solutions and then aliquotting samples for coulometric analysis. In this way, only the column effluent would be measured and losses of material during purification would have no effect on the final results.

In addition to reducing the sources of error for the plutonium assay measurement, bulk ion exchange of each solution enabled NBL to produce a high-purity CRM. Elemental impurities present in each of the separated isotope solutions prior to purification were identified using spark source mass spectrometry (SSMS). The results are discussed in Section VII.A. An ion-exchange technique was then specifically developed to remove these potentially interfering elements. Purity of the individual CRM units following ion-exchange clean-up was again verified using SSMS. The resulting high-purity product was deemed suitable for in-situ dissolution and use without excess handling on the part of the user.

A bulk ion-exchange procedure, capable of purifying up to 1.5 g total plutonium, was developed using a modification of NBL's current nitrate anion-exchange technique.[9,10] A plastic macro-column, 32 cm long, with a porous frit on the bottom, was designed by NBS and could accommodate up to 100 mL of resin. The plutonium solution was valence-adjusted using H_2O_2, in order not to

add any interfering or impurity ions such as iron, and loaded onto the column in 8 N HNO_3 (up to 600 mL). The purified plutonium fraction was then eluted using a dilute HCl-HF mixture. Figure 12 shows a macrocolumn loaded in 8 N HNO_3 with the plutonium visible as a dark (green) band on the top portion of the resin.

A major concern with the bulk ion-exchange was the stability of the solubilized Pu(IV) species, after removal from the ion-exchange column. The purified Pu(IV) must remain in solution for at least one day following removal from the column to allow for dilution and weight aliquotting of the CRM and chemical assay portions. The possibility thus existed for Pu(IV) in solution to disproportionate to Pu(III) and Pu(VI) during this time period. The NBL CPC assay of plutonium does not measure the Pu(VI) species, so that significant disproportionation would be expected to cause erratic results, biased low with regard to the "true" assay value.

A study using NBS SRM 949f was designed to evaluate the ion-exchange separation and the stability of the Pu(IV) species removed from the column. One unit of NBS SRM 949f was dissolved and put through the macrocolumn ion-exchange separation using $FeSO_4$ as the reducing agent. The purified plutonium was diluted with concentrated HNO_3 to a resulting acid concentration of 8 N HNO_3 with traces of HCl and HF. (Highly acidic nitrate solutions such as this tend to stabilize the Pu(IV) species.) The solution was then subsplit into 49 aliquots for coulometric analysis. Small quantities (~1 mL) of H_2SO_4 were added to each aliquot to complex Pu(IV) in the solution. These samples were allowed to remain in solution for up to 24 days after ion exchange before they were dried and analyzed using CPC. The formation of Pu(VI) in these solutions would be evidenced by

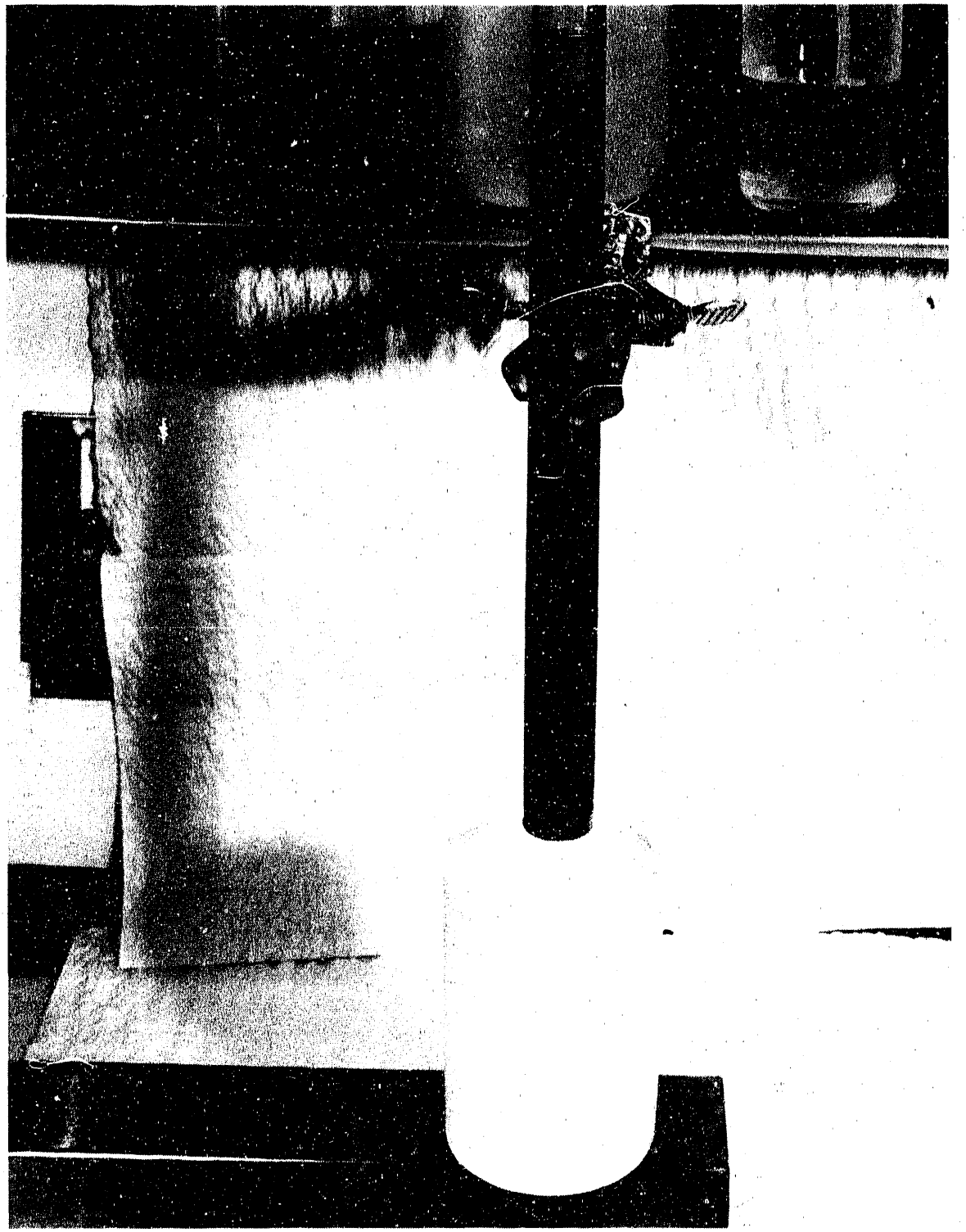

Figure 12. Macrocolumn for Bulk Ion Exchange of Plutonium

significantly lower recoveries for samples which had remained in solution form for the longest time period. Results of this evaluation are shown in Table II.

TABLE II

Bulk Ion-Exchange Study Using NBS SRM 949f

Group	Days After Ion Exchange	Mean Recovery using CPC	%RSD
1	0	100.024%	0.034%
2	0	100.025%	0.023%
3	3	100.025%	0.052%
4	6	100.022%	0.027%
5	10	100.035%	0.044%
6	13	100.017%	0.039%
7	17	100.033%	0.044%
8	20	100.051%	0.042%
9	24	100.021%	0.055%
		$\bar{x}$: 100.028%	

The NBS syringe method previously described in Section IV was used to aliquot the samples designated as Group 1. A 250-mL plastic wash bottle was used to aliquot the samples designated as Group 2. Following prescribed NBL procedures, these samples were aliquotted and assayed immediately following ion exchange. No significant difference in the mean recovery of plutonium was observed (<0.002%). The NBL squeeze bottle technique was chosen to aliquot the remaining sample groups over a 24-day period following anion-exchange purification. Excellent stability of the Pu(IV) was observed, as demonstrated by the reproducibility of the recovery (a relative uncertainty of less than 0.01% at the 95% confidence level). Another observation of this experiment was that a slight bias was evident. One explanation is that the presence of iron in the purified plutonium would create a positive bias, as iron is concurrently oxidized with plutonium, making an excess of plutonium seem to exist. This phenomenon is

not of great concern, since this study was performed for the strict purposes of evaluating the precision of the controlled-potential coulometric assay and detecting any differences in recovery due to the stability of the Pu(IV) oxidation state.

(Note: The effects of a bias in the coulometric measurement are negligible since only relative Pu-239 and Pu-242 content values were important, as previously stated in Section II.)

C. Sample Equilibration and Filament Temperature Study

A state of isotopic equilibrium exists when the component isotopes of an element are in the same chemical oxidation state. If such an equilibrium does not exist, then preferential adsorption of one isotope over another can occur during chemical purification, compromising the integrity of the isotope ratio values.

A study was implemented to evaluate the equilibration and measurement behavior of the CRM with respect to its oxidation state(s). Although equilibration had been performed on the separated isotopes used to produce the CRM as well as on the CRM itself, this study was considered necessary to determine the rigorousness and adequacy of the equilibration technique used and its effect, if any, on the measurement process.

Isotopic measurements were made on untreated and chemically-treated samples using the NBL mass spectrometer previously described. The two sample sets were then analyzed at a low and a high operating temperature of the sample filaments, as monitored by the signal intensity. Low-temperature analyses represented the operation of the sample filament at 800°C; the high temperature represented a sample filament temperature of 1200°C. By comparing the sample data generated at each

operating temperature, it could then be determined whether or not chemical treatment had a significant influence on the value of the measured isotope ratios.

The procedure for preparing the untreated and chemically-treated samples is described as follows. The contents of one CRM unit were dissolved in 8 N HNO_3 and three aliquots prepared. One aliquot was taken to incipient dryness and redissolved in 1 N HNO_3. The second aliquot was purified according to the NBL anion-exchange purification procedure. This procedure requires the use of $FeSO_4$ for valence adjustment of all plutonium to Pu(III), followed by oxidation to Pu(IV) using 15 N HNO_3. The plutonium was then adsorbed on Dowex 1(X-2) anion-exchange resin in 8 N HNO_3 media, the impurities removed by washing the resin with 8 N HNO_3, and the plutonium eluted using a dilute HCl-HF acid mixture. After elution and evaporation to dryness, the plutonium was redissolved in 1 N HNO_3. A third aliquot was also purified by the anion-exchange technique; however, no valence adjustment was performed. These three sample aliquots were then re-identified as "untreated," "equilibrated/ion exchanged," and "ion exchanged" respectively.

Approximately 100 ng of sample were selected for each analysis, loaded onto degassed rhenium filaments, oxidized by electrical resistance heating, and mounted into the mass spectrometer. A total of 36 analyses (12 per sample) were made at the low-temperature and high-temperature filament temperatures according to the following procedure.

Certain individual ratios were deleted from the calculation of the mean of each ratio set due to outlier criteria based upon tests for skewness, kurtosis, and Dixon's t-test already incorporated in the data acquisition's software. When outliers were detected, they were eliminated and means recalculated for each ratio set along with the appropriate relative standard deviations.

Time from start of analysis (min.)	Description of Procedure
0-1	(Low-temperature procedure) The ionizing filament adjusted to 2140°C and the sample filament at 1.0 A.
5	The sample filament currents increased to yield a $1 * 10^{-12}$ A (100 mV) Pu^+ grid signal and the ionizing filament readjusted to 2140°C.
10	The sample filament currents increased to yield a $3 * 10^{-12}$ A (300 mV) Pu^+ grid signal.
15	The sample filament current increased to yield a $4 * 10^{-12}$ A (400 mV) Pu^+ grid signal.
20	The ionizing filament readjusted to 2140°C and sample filament current readjusted to maintain a $4 * 10^{-12}$ A Pu^+ grid signal.
25-30	Data acquisition begins for the low-temperature procedure. Baseline measurements are taken, then peak measurements are initiated. Three ratio sets are taken; each set comprised of 8 scans generating 15 individual ratio values. The mean of the 15 individual ratio values is calculated, a grand mean for the three set means is generated, and the precision (in terms of relative standard deviation) is determined. The measurements concluded after 10 minutes.
35-40	(High-temperature procedure) The sample filament increased to yield a $1 * 10^{-11}$ A (1 V) Pu^+ grid signal. The ionizing filament rechecked and, if necessary, readjusted to 2140°C.
45-50	Data acquisition begins. Data collection identical to the low-temperature protocol.

Table III gives the low-temperature and high-temperature results for these studies. The only observed bias was the temperature and mass dependent fractionation factor related to the ionization and thermal behavior in the source. The data indicated that no treatment-to-treatment differences existed between samples. The studies verified the supposition that the CRM is isotopically

equilibrated. Of equal importance was the finding that the CRM can be processed through the same chemistry as "unknown" plutonium material without loss of integrity.

TABLE III

Effect of CRM Sample Treatment on Measured Isotopic Ratios

Uncorrected Pu-242/Pu-239, (%RSD of set)

LOW TEMPERATURE

Filament Loading	Untreated	Ion Exchanged	Equilibrated/ Ion Exchanged
1	0.998776 (0.008)	0.999474 (0.001)	0.998217 (0.027)
2	0.999018 (0.007)	0.998289 (0.041)	0.997850 (0.014)
3	0.998065 (0.016)	0.997892 (0.003)	0.998943 (0.032)
4	0.997753 (0.003)	0.999016 (0.050)	0.997813 (0.026)
5	0.997914 (0.002)	0.998618 (0.005)	0.998548 (0.025)
6	0.998610 (0.019)	0.998757 (0.023)	0.998206 (0.005)
$\bar{x}$:	0.998356	0.998674	0.998263
%RSD:	0.051	0.055	0.043

HIGH TEMPERATURE

Filament Loading	Untreated	Ion Exchanged	Equilibrated/ Ion Exchanged
1	0.999070 (0.002)	0.999448 (0.017)	0.999136 (0.012)
2	0.999798 (0.032)	0.998183 (0.013)	0.999471 (0.012)
3	0.998862 (0.008)	0.999034 (0.020)	0.999542 (0.011)
4	0.998737 (0.021)	0.999046 (0.042)	0.999414 (0.012)
5	0.998270 (0.009)	0.999239 (0.005)	0.998927 (0.007)
6	0.998478 (0.008)	0.998825 (0.030)	0.999487 (0.009)
$\bar{x}$:	0.998869	0.998963	0.999330
%RSD:	0.054	0.044	0.024

D. Effect of Sample Size on the Isotope Ratio Value Study

A critical parameter to control in the thermal ionization process is the amount of sample undergoing vaporization and ionization. By careful control of the rate and amount of fractionation taking place, the mass spectrometer operator can better reproduce

measured isotope ratio values. This is achieved by placing all measurements on the same point on the fractionation curve where the corrections are most similar.

The following study was performed to determine to what extent sample size differences might impact on the measured isotope ratio values. This study consequently provided insight as to how much of a sample size difference could be tolerated in order to minimize sample-to-sample effects on the overall measurement uncertainty. Previous work had demonstrated that sample sizes of 70- to 100-ng plutonium provide sufficient Pu^+ signal intensity to negate or minimize electronic circuitry instability and ion intensity stability effects which can degrade the precision of the measured isotope ratio. A study was therefore conducted using sample sizes of 70-, 85-, and 100-ng to evaluate the magnitude of fractionation bias in the measured isotope ratio with respect to sample size.

A low-temperature sample filament procedure was used in making these measurements. Due to the intent of this study and the information provided in the sample treatment study previously discussed, there was no indication that dual (low and high) temperature measurements were necessary, nor that any chemical treatment should be performed. Therefore, each sample analyzed came directly from a CRM aliquot taken from the CRM bottle, with no chemical treatment performed. Table IV details the results obtained from this study.

As can be seen in Table IV, significant differences were observed among the three sample sizes analyzed. It is evident that 20+% variations among sample sizes can create biases of 0.02-0.04% in the measured ratios. It was therefore concluded that strict control of the sample quantity had to be maintained within the few percent uncertainty limits of the microsyringe used for sample solution loading onto the filament.

TABLE IV

Effect of Sample Size on Measured Isotopic Ratio of CRM

Uncorrected Pu-242/Pu-239, (%RSD of set)

LOW TEMPERATURE

Filament Loading	70-ng Pu sample size	85-ng Pu sample size	100-ng Pu sample size
1	0.999023 (0.036)	0.999417 (0.005)	0.998660 (0.025)
2	0.999375 (0.013)	0.999087 (0.014)	0.998953 (0.014)
3	0.999128 (0.030)	0.998439 (0.029)	0.998674 (0.003)
4	0.999691 (0.014)[a]	0.999090 (0.003)	0.998586 (0.017)
5	0.999074 (0.013)	0.998894 (0.013)	0.998224 (0.017)
6	0.998966 (0.027)	0.999063 (0.009)	0.998338 (0.003)
$\bar{x}$:	0.999113	0.998998	0.998573
%RSD:	0.016	0.032	0.026

[a]Outlier.

VI. DEVELOPMENT OF THE GENERAL ANALYTICAL PROCEDURE TO BE USED FOR THE MASS SPECTROMETRY CERTIFICATION MEASURMENTS

Results obtained from the sample equilibration, sample filament temperature, and sample size studies on the mass spectrometric measurements were evaluated to determine the best procedure to use for the certification measurements. The low-temperature procedure is generally favored when isotope ratios of low dynamic ranges are being measured. This is because operating at high temperatures often produces an increased rate of fractionation which can result in systematic differences between sample analyses. Although this phenomenon was not readily apparent in the data found in Table III, no assumption was made that it does not exist. Comparisons of data from the three aforementioned studies suggested that low-temperature analysis of 100-ng sample sizes of untreated sample solutions would be acceptable for certification work. Data presented in Table V verify these parameters. Agreement between

the three sources of data in this table, on the order of one part in 10^4, indicates that this procedure yields results which are reproducible enough for the certification work.

TABLE V

Summary of Data From the Sample Treatment and Sample Size Studies (100-ng sample sizes)

Source of Data	$\bar{x}$, uncorrected Pu-242/Pu-239	%RSD	Percent Relative Difference from Overall Mean
Table III: All data	0.998431	0.021	-0.002%
Table III: "Untreated" "Low-Temperature" Sample data	0.998356	0.054	-0.010%
Table IV: "100-ng" Sample data	0.998573	0.026	+0.012%
Overall Mean:	0.998453		

VII. EVALUATION OF THE EFFECT OF IMPURITY LEVELS ON ISOTOPIC MEASUREMENTS

A. Impurity Analysis of the Separated Isotope Solutions

SSMS measurements performed by ORNL on NBL solution samples of the separated isotopes, revealed the presence of a number of impurities at concentration levels which can interfere with TIMS and coulometry. An anion-exchange method capable of purifying "large" amounts of plutonium was therefore evaluated to determine its effectiveness in reducing the impurity levels in the individual isotope bulk quantities needed to prepare the CRM. This is described in Section V.B. Accordingly, 1-g plutonium capacity anion-exchange macrocolumns were prepared to use for purification of 0.9-g quantities of each of the separated plutonium isotopes. The solutions were then purified

in a two-stage process to maximize impurity removal, and 10-mg samples sent to ORNL for SSMS analysis. As shown in Table VI, significant reductions in the impurities present in the separated isotopes were achieved by the anion-exchange method.

B. Impurities-Doping Experiment

An investigation as to the influence of the impurities remaining in the purified solution on mass spectrometry was conducted. This experiment was performed prior to the production of the CRM to determine what levels of impurities could be tolerated without adversely affecting the precision and accuracy of the measured ratio. NBS SRM 947 was used as the test material.

Purified NBS SRM 947 was "doped" with specific impurities at two concentration levels. A third concentration level was the purified NBS SRM 947 itself, considered the "control" sample. The six major impurity elements, Al, Fe, K, Ni, S, and Th, found in the purified separated isotopes were added to two aliquots of NBS SRM 947 in the form of salts of the elements. High-purity salts containing trace levels of impurities were dissolved in high-purity acids and added to the SRM aliquots. The additions were to closely resemble the "predicted" impurity levels of the equally blended separated isotopes, as determined from the impurities analyses of the purified isotopes given in Table VI. These predicted levels are in Table VII. Table VIII shows imputities content of the "doped" NBS SRM 947 materials, as determined by known additions of the metal salts.

TABLE VI

Spark Source Mass Spectrometry Results
for Separated Isotope Materials*

Element	Before Purification		After Purification	
	Pu-239, µg/g	Pu-242, µg/g	Pu-239, µg/g	Pu-242, µg/g
Ag	<1	<1	<1	
Al	≥600	10	100	40
As	7	<0.1	7	<0.1
B	20	20	0.8	0.3
Ba	7	50	7	50
Bi	<0.4	<0.7		
Ca	20	20	6	1
Cd	<2	<2		
Ce	3	<0.3		
Cl	500	100		
Co	30	4		
Cr	200	3	10	1
Cs	<0.1	<0.1		
Cu	500	2		
Fe	≥4000	30	60	20
Ga	<0.3	<0.3		
In	0.2	<0.2		
K	700	10	20	5
La	7	2		
Mg	20	10	3	<2
Mn	30	<1	0.5	<1
Mo	<3	<1	<3	<1
Na	70	30	10	7
Nb	<0.7	<0.3		
Ni	200	70	20	90
P	50	6	4	1
Pb	30	6		
Pd	<1	<1		
Rb	<0.1	<0.1		
Rh	<0.2	<0.2		
Ru	<1	<1		
S	200	300	100	50
Si	<3	<3	10	<4
Sn	<1	<1		
Sr	<0.1	1		
Th	50	<2	40	8
Ti	20	<3		
V	<0.4	<0.4		
Zn	20	2		
Zr	<0.4	4		

*Measurements made at ORNL. No listed value indicates non-detectable quantities; 0 µg/g assumed.

TABLE VII

Predicted Impurity Levels For NBL CRM 128

Element	After Purification Pu-239, µg/g	Pu-242, µg/g	Predicted Impurity µg/g
Al	100	40	70
Fe	60	20	40
K	20	5	13
Ni	20	90	55
S	100	50	75
Th	40	8	24
		Total:	277

TABLE VIII

Major Impurities Content of the "Doped" NBS SRM 947

Element (Matrix)	NBS SRM 947 Pu wt,g #1 Aliquot	#2 Aliquot	Elemental Impurity added,µg #1 Aliquot	#2 Aliquot	Elemental Concentration,µg/g #1 Aliquot	#2 Aliquot
Al (as $AlCl_3 \cdot 6H_2O$)	0.0502	0.0495	5	25	100	505
Fe (as $FeSO_4 \cdot 7H_2O/H_2SO_4$)	0.0502	0.0495	3	15	60	303
K (as KCl)	0.0502	0.0495	1	5	20	101
Ni (as $NiCl_2 \cdot 6H_2O$)	0.0502	0.0495	4.5	22.5	90	455
S (as $FeSO_4 \cdot 7H_2O/H_2SO_4$)	0.0502	0.0495	4.6	23	92	465
Th (as $Th(NO_3)_4 \cdot 12H_2O$)	0.0502	0.0495	1	5	20	101
				Total:	382	1930

Aliquot #1 of the NBS SRM 947 material was prepared to resemble the impurity characteristic of the equally-blended separated isotopes based upon the SSMS "Pu-239 after purification" data given in Table VI. Aliquot #2 of the NBS SRM 947 material was doped with approximately five times the impurities as the first aliquot to observe what effect this high level of impurities would have on the mass spectrometric measurement.

The two doped aliquots and the control materials were isotopically analyzed using TIMS. The results of the analysis are shown in Table IX.

TABLE IX

Mass Spectrometric Results of the Impurities Doping Experiment

Sample/Aliquot	Impurities Level (from Table VIII)	Pu-240/Pu-239	%RSD
NBS SRM 947 - 1	382 µg/g	0.241032	0.034
NBS SRM 947 - 2	1930 µg/g	0.240981	0.026
NBS SRM 947 - 3	Control	0.240980	0.027
	$\bar{x}$:	0.240998	

No distinguishable differences with respect to precision between doped and control materials were observed. The conclusion was drawn that the impurity levels of the CRM would not affect the precision and accuracy of the isotopic measurements, nor interfere with the behavior of the material during thermal ionization.

VIII. PRODUCTION OF THE CERTIFIED REFERENCE MATERIAL

A. Dissolution and Aliquotting of the Separated Isotopes

The Pu-239 and Pu-242 separated isotope starting materials were obtained from the ORNL Isotope Sales Division. The ORNL Batch Number designation for the Pu-239 was "Pu 239 277-M"; the Pu-242 designation was "Pu 242 327-A." The materials were solid samples, the Pu-239 a metal and Pu-242 an oxide powder. Approximately 5.0 g of the Pu-239 metal and 5.7 g of the Pu-242 oxide (~5.0 g Pu) were obtained.

The badly oxidized Pu-239 was subjected to the electrochemical cleaning process (described in Section V.A.) to remove the oxidized coating. Pre-cleaning and post-cleaning weighings indicated a 4% decrease in the weight of the metal, attributable to the removal of the oxides from the metal surface (see Table X). The dissolution of the metal was

performed using 25 mL of a metal dissolver solution (prepared from 50 mL HCl, 6 mL HNO_3, and 200 µL HF diluted to 100 mL using distilled, deionized water) followed by gentle heating and digestion with 15 mL HCl, 500 µL HF, and 25 mL 8 N HNO_3 added to insure total dissolution. The Pu-242 oxide powder was light green and was free-flowing. Dissolution was performed in 200 mL 8 N HNO_3 containing 50 µL HF. All acids used were NBS quartz-distilled high-purity acids.

The dissolved isotopic solutions were further diluted to final concentrations of approximately 0.009 g Pu/g soln from which aliquots were taken for assay, isotopic, and impurities analyses as well as blending to create the actual CRM. Table X details the dissolution and aliquotting of the materials.

TABLE X

Dissolution and Aliquotting of Separated Isotope Materials

Dissolution

Separated Isotope	Pre-cleaning Weight, g Pu	Post-cleaning Weight, g Pu	Dilution Wt.,g	Concentration, g Pu/g soln
Pu-239 metal	4.97298	4.77375	557.6618	0.008560
Pu-242 oxide	5.00417[a]	--[b]	576.0793	0.008687

Aliquotting

	Pu-239 Solution		Pu-242 Solution		
Aliquot No.	Solution Weight, g	Pu taken, g	Solution Weight, g	Pu taken, g	Purpose
1	0.6680	0.005718	0.6286	0.005461	Isotopic[c]
2	1.2233	0.010471	1.1978	0.010405	Impurities[d]
3	0.5876	0.005030	0.5930	0.005151	Isotopic[c]
4	1.3306	0.011390	1.2282	0.010669	Assay[e]
5	98.5428	0.84353	95.7758	0.83197	CRM

[a]Calculated assuming stoichiometric PuO_2; Pu/PuO_2 = 0.8832; total PuO_2 = 5.66595 g.
[b]No cleaning performed on oxide.
[c]Thermal ionization mass spectrometry.
[d]Spark source mass spectrometry.
[e]Isotope dilution mass spectrometry.

B. Preliminary Analyses of Separated Isotope Solutions

The aliquot for assay of each of the separated isotope solutions by isotope dilution mass spectrometry (IDMS) was taken to assure that the calculated concentrations were close to the target concentrations. These samples were spiked with NBS SRM 996 (Pu-244 Spike Assay and Isotopic Standard) and analyzed. These measurements verified the approximation made for the target concentration for each solution. Results of the impurities analysis of each solution were given in Table VI and discussed in Section VII.A.

Two aliquots of each solution were taken for isotopic analyses by TIMS. The two aliquots were "split" into two samples and subjected to the anion-exchange process for purification. The high-temperature procedure (described in Section V.C) was used to more accurately measure the minor isotopes. Table XI gives the results of these measurements. Mass spectrometric bias was corrected by concurrent analysis with NBS SRM 948 (Plutonium Isotopic Standard, 92% Pu-239). However, due to the high isotopic purity of each isotope, bias corrections applied had a negligible effect on the isotopic values of the materials.

The uncertainties stated for the major isotope of each isotope material were less than 0.003%. Although the analysis of the isotopic materials using the high-temperature procedure resulted in a higher rate of fractionation due to the higher rate of evaporation of the sample material, the consequently greater imprecision was smaller than the imprecision attributable to the magnitude of the ratios being measured ($1*10^{-5}$ to $5*10^{-4}$).

TABLE XI

Isotopic Distribution of the Separated Isotopes

Decay-corrected to 10/1/84

Pu-239 Metal

Isotope:	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Pu-244
Weight Percent:	0.0030	99.8978	0.0491	0.0409	0.0092	-
Std. Deviation:	0.0005	0.0029	0.0004	0.0014	0.0006	-
95% Conf Interval:	±0.0004	±0.0026	±0.0004	±0.0013	±0.0005	-

Pu-242 Oxide

Isotope:	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Pu-244
Weight Percent:	0.0043	0.0051	0.0212	0.0308	99.9376	0.0010
Std. Deviation:	0.0007	0.0007	0.0015	0.0017	0.0039	0.0003
95% Conf Interval:	±0.0005	±0.0005	±0.0011	±0.0012	±0.0028	±0.0003

C. Preparation of the Certified Reference Material and Assay Samples

Two aliquots of each isotope solution containing approximately 0.8 g Pu each were purified using the anion-exchange procedure with the macrocolumn described in Section V.B. A second anion exchange was performed to further remove any impurities not eluted as efficiently during the first anion exchange. The purified plutonium solutions were then diluted to a weight of 560 g for aliquotting. Samples were aliquotted using the NBS syringe described in Section IV.A. The first aliquots taken were for IDMS assay and an isotopic content recheck necessary to estimate the amounts of each isotope solution which would be required to yield a Pu-242/Pu-239 ratio of unity within the desired range of one part in one thousand (0.10%). Next, the coulometric assay samples were taken which would allow for the calculation of a Pu-242/Pu-239 ratio of the CRM based upon

weight aliquotting and CPC assay data. These samples were taken before and after the large (~400 g) aliquot which would be used to produce the CRM itself. This was to insure that any change in concentration occurring over the time interval of the aliquotting could be evaluated.

Table XII gives the aliquotting and coulometric assay data described. Note that the large aliquots taken to blend the CRM are denoted "239" and "242" for the Pu-239 and Pu-242 isotopic solutions, respectively.

TABLE XII

Aliquotting and Coulometric Data for the Preparation of Assay and CRM Samples

Dates of analyses: 8/19,22/83; 9/14,15/83

Pu-239 Solution			Pu-242 Solution		
Aliquot No.	Aliquot wt., g	Pu Assay mg/g	Aliquot No.	Pu Aliquot wt., g	Assay mg/g
1	6.8696[a]	--	1	5.7995[a]	--
2	6.9227[a]	--	2	7.0937[a]	--
3	7.2258[a]	--	3	7.9721[a]	--
4	6.39300	1.43229[b]	4	7.16358	1.45481
5	7.14240	1.43283	5	6.89920	1.45408
6	7.48553	1.43276	6	7.07567	1.45437
7	7.23174	1.43310	7	6.74274	1.45436
8	6.58325	1.43303	8	7.06857	1.45444
9	7.28110	1.43287	9	6.94649	1.45437
"239"	384.1705		"242"	383.3478	
10	6.75638	1.43275	10	7.12908	1.45447
11	6.65900	1.43295	11	6.93194	1.45456
12	6.90748	--[c]	12	7.12058	--[c]
13	6.91667	1.43305	13	6.87472	1.45446
14	6.72436	1.43303	14	7.31543	1.45448
15	6.86992	1.43282	15	6.77685	1.45431
	$\bar{x}$:	1.43292			1.45443
	RSD%:	0.009(n=10)			0.011(n=11)
Decay Adjusted Value to 10/1/84:		1.43285			1.45441

[a]Assay samples taken for IDMS for preliminary concentration calculations only; data not included in CRM gravimetric isotopic value determination.
[b]Statistical outlier; value deleted from mean calculation.
[c]Sample lost due to electrical problems with the coulometer.

Table XIII gives quality control information as to the performance of the coulometer used for assay measurements. NBS SRM 949f (Plutonium Metal Assay Standard) was used as the standard material. The data list the weight recovery of the plutonium relative to the certified value for the NBS SRM 949f standard analyzed. These quality control standard samples were analyzed concurrently with assay samples of the isotope solutions, previously described and detailed in Table XII.

TABLE XIII

NBS SRM 949f Plutonium Metal Coulometric Assay Data

Dates of Analyses: 8/19,22/83; 9/14,15/83

Standard No.	Pu, mg taken	Pu, mg found	Relative Difference, %
"A"	7.4559	7.4565	+0.008
"B"	8.5374	8.5415	+0.048
"C"	9.7952	9.7945	-0.007
"D"	8.0429	8.0443	+0.017
"E"	10.2212	10.2181	-0.030
"F"	8.6029	8.6016	-0.015
"H"	9.4653	9.4665	+0.013
"I"	10.9011	10.8994	-0.016
"J"	8.2182	8.2161	-0.025
		$\bar{x}$:	-0.001
		s:	0.025

The 383.3-g aliquot of the Pu-242 isotope solution ("242") was directly added to the 384.2-g aliquot of the Pu-239 isotope solution ("239") contained in a 1-L TFE-fluorocarbon bottle to produce the CRM bulk material. Preliminary IDMS measurements, incorporated with the isotopic data of each isotope, indicated that these solution weights would provide a ratio of one, to an accuracy of one part in a thousand (0.10%).

Thorough solution mixing and a final equilibration were performed on the bulk solution prior to aliquotting into individual reference material units. Several mL of H_2O_2 were added to the solution, the bottle wrapped in heavy gauge aluminum foil, and placed on a hot plate and heated at 80°C for four hours for a final equilibration. The solution was then removed from the heat and allowed to cool to room temperature for two hours. Finally, the bottle was tightly capped and vigorously shaken for several minutes. The bottle was then stored for several days prior to final aliquotting, due to scheduling requirements.

The individual CRM aliquots were taken using a Drummond repeating pipette and a Mettler AE163 top-loading balance with printer. The aliquotting apparatus resembled that shown in Figure 8. The CRM aliquots, containing 1 mg of plutonium each, were dispensed into 997 30-mL bottles, which became the primary containment for each reference material unit. An exact weight, to ±0.2 mg, was taken to insure that no large variation of plutonium content existed between units. The use of the pipette and balance allowed for a sampling reproducibility of ±3%. Since the aliquotting of all the units occurred within a 12-hour period, no substantial solution concentration change took place that could appreciably impact on the plutonium content of the units prepared at the end of the aliquotting.

The aliquots were taken to dryness by heating the bottles using heating blocks. One such block is shown in Figure 13. Six of these blocks, each designed to hold 12 bottles, allowed for 72 units to be dried at a time. Since each unit required four to six hours for complete drying to a nitrate, the entire drying process took 96 hours to complete.

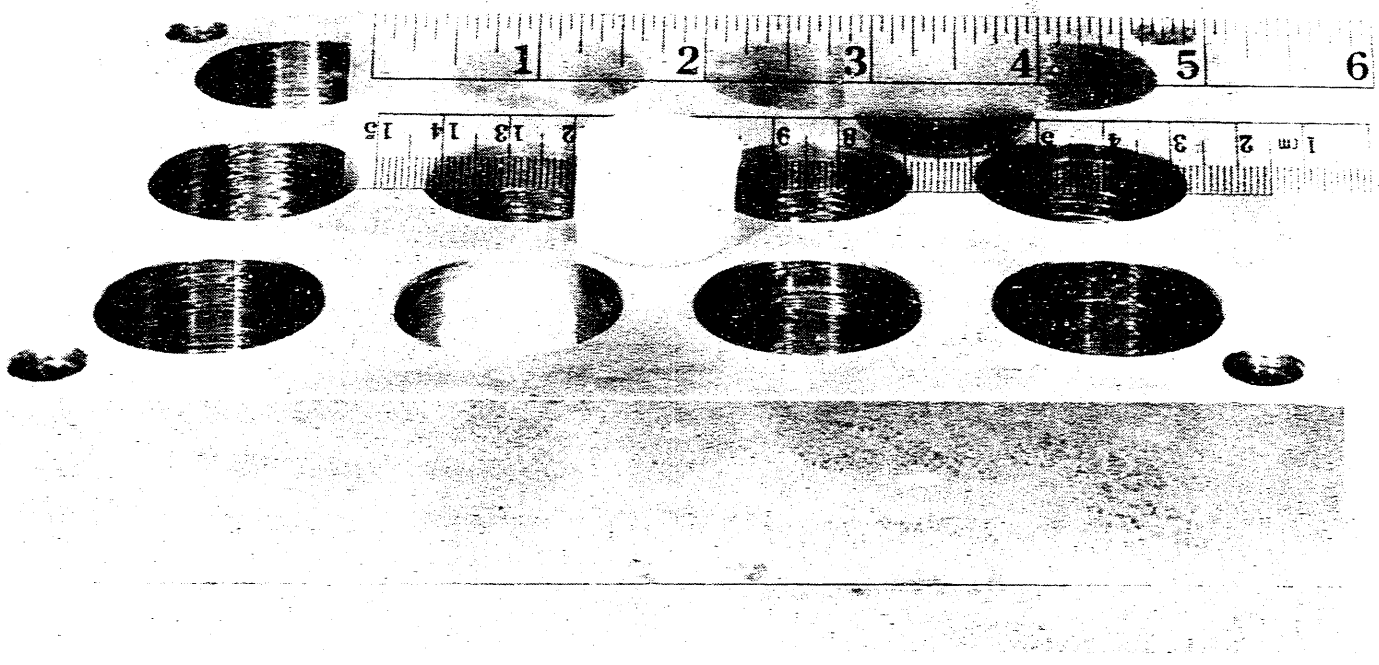

Figure 13. Heating Block for Drying CRM Units

Upon drying, the bottles were removed from the blocks, cooled, capped, and labeled. Finally, the bottles were placed in small plastic bags which were then heat-sealed. Each bottle, containing a unique weight of plutonium, was coded to allow for traceability of the unit to its specific weight for accountability and informational purposes if requested by the purchaser and/or user.

D. Gravimetric Calculation of NBL CRM 128 Pu-242/Pu-239 Value

The Pu-242/Pu-239 ratio of the CRM, determined gravimetrically, was calculated from the isotopic analysis of the separated isotopes (Table XI), moles of plutonium from each separated isotope solution determined from the assay (Table XII) and weight of the "239" and "242" solutions taken. Equation 1 was used in the atom ratio calculation.

$$\text{atom ratio } \frac{\text{Pu-242}}{\text{Pu-239}} \text{ of CRM} = \frac{\text{moles Pu-242 in "239" + moles Pu-242 in "242"}}{\text{moles Pu-239 in "239" + moles Pu-239 in "242"}} \quad (1)$$

Data for the calculation and the result are shown in Table XIV.

TABLE XIV

Calculation of Pu-242/Pu-239 Atom Ratio for NBL CRM 128 (Based Upon Gravimetric Data)

Decay-corrected to 10/1/84

Isotope Solution	Solution Weight, g	Pu-239, mmoles	Pu-242, mmoles	Atom Ratio Pu-242/Pu-239
"239"	384.1705	2.30032	0.000209	
"242"	383.3478	0.000119	2.30191	1.00073

IX. PROVISIONAL CERTIFICATION MEASUREMENTS

A. Sample Preparation

Mass spectrometric measurements on selected units of the CRM were made using NBS SRM 947 (78% Pu-239) as the calibration material. This provided a means of establishing the certified value of the CRM relative to existing plutonium isotopic standards until the preparation of calibration mixtures and associated measurements could be performed.

Aliquots from three subsamples of NBS SRM 947 supplied as the plutonium sulfate tetrahydrate salt, designated 947-1, 947-2, and 947-3, were dissolved in 8 $\underline{N}$ HNO_3 and anion exchanged to remove fixed and ingrowing impurities prior to mass spectrometric analysis. The purified solutions were diluted to a plutonium concentration of 33 µg/mL in 1 $\underline{N}$ HNO_3. Eight selected units of the CRM were diluted in 1 $\underline{N}$ HNO_3 to a concentration equivalent to the NBS SRM 947 solutions. The eight units chosen were those numbered 001, 144, 287, 447, 573, 724, 855, and 996.

Approximately 3 µL of sample solution, containing about 100 ng of plutonium, were placed on a single degassed sample filament and dried by electrical resistance heating at a low current (0.5 A) to a solid nitrate. (A microsyringe/pipette was used to dispense the sample solution onto the sample filament.) The current was increased to 1.8 A for 30 seconds to drive off any remaining moisture and oxidize the plutonium. This filament was then mounted into an assembly opposite a blank sample filament. A third ionizing filament was placed in position and the assembly inserted into the mass spectrometer for analysis.

B. Analytical Protocol

The procedure described in Section V.C. was used for the analyses. The analytical scheme (Figure 14, read top to bottom, starting from left) was chosen not only to bracket the "unknown" CRM isotope ratios with the NBS SRM 947 ratios, but to help monitor any day-to-day or sample-to-sample differences in measurement performance.

947-1	Unit #447	947-3	Unit #573
Unit #001	947-3	Unit #001	947-1
947-2	Unit #447	947-2	Unit #447
Unit #996	947-3	Unit #001	947-1
947-3	Unit #573	947-1	Unit #001
Unit #855	947-2	Unit #996	947-2
947-3	Unit #287	947-1	Unit #287
Unit #144	947-1	Unit #855	947-3
947-2	Unit #724	947-2	
Unit #724	947-1	Unit #144	
947-1	Unit #144	947-3	
Unit #287	947-2	Unit #724	
947-1	Unit #855	947-3	
Unit #573	947-3	Unit #287	
947-2	Unit #996	947-2	
			TOTAL: 53

Figure 14. Provisional Certification Measurements Scheme

C. Results of Provisional Certification Measurements

The provisional certification data are given in Table XV. The certified Pu-240/Pu-239 ratio of NBS SRM 947 was used to establish the Pu-242/Pu-239 ratio of the CRM. All values listed are measured values which are uncorrected for instrument bias effects.

TABLE XV

Provisional Certification Measurements Using Mass Spectrometry

Decay-corrected to 10/1/84

NBS SRM 947 Analyses

Aliquot No.	Analysis No.	Measured Pu-240/Pu-239	Mean	%RSD
947-1	1	0.241271		
	2	0.241158		
	3	0.241154		
	4	0.241054		
	5	0.241197		
	6	0.241195		
	7	0.241060		
	8	0.241229		
	9	0.241133	0.241161	0.030
947-2	1	0.241156		
	2	0.241208		
	3	0.241060		
	4	0.241064		
	5	0.241045		
	6	0.241092		
	7	0.241196		
	8	0.241082		
	9	0.241075	0.241109	0.026
947-3	1	0.241153		
	2	0.241053		
	3	0.241058		
	4	0.241187		
	5	0.241138		
	6	0.241192		
	7	0.241104		
	8	0.241295		
	9	0.241135	0.241146	0.030
		$\bar{x}$:	0.241139	
		%RSD:	0.011	

TABLE XV (Cont.)

NBL CRM 128 Analyses

Unit No.	Analysis No.	Measured Pu-242/Pu-239	Mean	%RSD
#001	1	0.998464		
	2	0.998323		
	3	0.998995	0.998594	0.035
#144	1	0.998385		
	2	0.998696		
	3	0.998290	0.998457	0.021
#287	1	0.998693		
	2	0.998486		
	3	0.998680	0.998620	0.012
#447	1	0.998389		
	2	0.998273		
	3	0.998149	0.998270	0.012
#573	1	0.998430		
	2	0.998915		
	3	0.998706	0.998684	0.024
#724	1	0.998449		
	2	0.998138		
	3	0.998128	0.998238	0.018
#855	1	0.998799		
	2	0.998671		
	3	0.998651	0.998707	0.008
#996	1	0.998883		
	2	0.998396		
	3	0.998166	0.998482	0.037
		$\bar{x}$:	0.998507	
		%RSD:	0.018	

D. Calculation of NBL CRM 128 Provisionally Certified Pu-242/Pu-239 Value and Associated Uncertainty

Table XVI gives the certified NBS SRM 947 value as well as the calculated correction factor (certified value/measured value), and its application to the CRM's measured Pu-242/Pu-239 ratio

to yield the corrected Pu-242/Pu-239 ratio. The adjustment of the correction factor determined from the one-mass difference in the Pu-240/Pu-239 ratio of NBS SRM 947 to the extrapolated three-mass Pu-242/Pu-239 ratio correction was made using the following general equation:

$$CR_{h/j} = (CR_{i/j} - 1) * (m_h - m_j) + 1 \qquad (2)$$

where: $CR_{h/j}$ = correction factor for the ratio of isotopes h and j (i.e., Pu-242 and Pu-239, respectively),

$CR_{i/j}$ = correction factor for the ratio of isotopes i and j (i.e., Pu-240 and Pu-239, respectively),

m_h = nuclide mass of isotope h (Pu-242), and

m_j = nuclide mass of isotope j (Pu-239).

Included in Table XVI is the error statement determined from all uncertainty components, including all random and systematic errors. An extrapolated uncertainty, based upon the known reproducibility of the mass spectrometer, was used to determine the relative 95% confidence interval (R_{CI}) of the provisional Pu-242/Pu-239 value using equation (3) below:

$$R_{CI} = [R_{SE}^2 + (K_{rep} * \frac{m_h - m_j}{m_i - m_j})^2]^{\frac{1}{2}} * Z_{(95\%)}, \qquad (3)$$

where: $R_{SE}^2 = (\frac{RSD}{N})^2$, the squared analytical relative error,

K_{rep} = ~0.01%, the known reproducibility of the mass spectrometer for the specific measurements,

$Z_{(95\%)}$ = 1.96, the 95% two-side critical value for the normal probability distribution, and

m_h, m_i, and m_j = the nuclide masses of isotopes h, i, j (Pu-242, Pu-240 and Pu-239 respectively).

TABLE XVI

Calculation and Statistical Evaluation of NBL CRM 128 Provisionally Certified Pu-242/Pu-239 Ratio Value

Decay-corrected to 10/1/84

Source/Measurement	Value	%RSD	95% Confidence Limit
NBS SRM 947 Certified Pu-240/Pu-239 Ratio	0.24137	--	0.10%
NBS SRM 947 Measured Pu-240/Pu-239 Ratio[a]	0.241139	0.011	--
Calculated Pu-242/Pu-239 Correction[b]	1.002873	--	--
NBL CRM 128 Measured Pu-242/Pu-239 Ratio[a]	0.998507	0.018	--
Corrected Pu-242/Pu-239 Ratio[c]	1.001376	0.061[d]	

[a]From Table XV.
[b]From Equation (2).
[c]Measured Pu-242/Pu-239 ratio multiplied by calculated Pu-242/Pu-239 correction.
[d]From Equation (3).

E. Isotopic Abundance Values for NBL CRM 128 Based Upon Provisional Certification Measurements

Table XVII gives the isotopic distribution of the CRM determined from the provisional certification measurements. Although the abundance values are not certified, these values are given for information purposes.

TABLE XVII

Isotopic Distribution of NBL CRM 128
(Provisional Certification Measurements)

Decay-corrected to 10/1/84

Isotope	Atom %
Pu-238	0.004
Pu-239	49.928
Pu-240	0.035
Pu-241	0.036
Pu-242	49.996
Pu-244	<0.001

X. ABSOLUTE CERTIFICATION MEASUREMENTS

A. Preparation of Calibration Mixtures

Calibration mixtures, containing accurately known quantities of the isotopes of Pu-239 and Pu-242, were prepared for use as standards for the absolute certification measurements on the CRM. These mixtures were prepared from the chemically and isotopically pure separated isotopes used to produce the CRM itself. The mass spectrometric analyses of these synthetic mixtures provided a bias correction which, when applied to the CRM sample being calibrated, allowed for an absolute ratio to be calculated for the sample.

Note: It is generally assumed that instrument bias is independent of isotopic composition when the measurement system is determined to be linear. Results obtained from the analysis of 10% to 90% enriched U-235 standards certified by the National Bureau of Standards (SRMs U100, U200, U500, and U900) indicated no nonlinearity in the mass spectrometer used for the certification work. Since nonlinearity would be insignificant

in measuring materials of similar isotopic composition, it was necessary to produce calibration mixtures with a range of isotopic compositions.

Approximately 0.25 g of each separated isotope was purified twice using a macrocolumn described in Section V.B. The eluted plutonium was diluted with 8 $\underline{N}$ HNO_3 to a weight of 250 g. Samples were aliquotted for IDMS assay and an isotopic content recheck to estimate the plutonium content of each isotopic solution prior to the aliquotting of the calibration mixtures.

Coulometric assay samples were taken, using the NBS syringe, which would provide the "true" gravimetric Pu-242/Pu-239 ratio of the calibration mixtures. As with the preparation of the CRM itself, described in Section VIII.C, these samples were taken before and after the aliquotting of the calibration mixtures to insure that no change in concentration occurred during the time interval of the aliquotting.

Between the first six and last six coulometric aliquots, five calibration mixture aliquots were taken. The desired Pu-242/Pu-239 ratios of each calibration mixture were to closely resemble and bracket the CRM ratio. The "target" ratios of these mixtures were 0.99:1, 0.995:1, 1:1.005, and 1:1.01, with the fifth mixture closely matching the actual CRM ratio to within a few parts in one thousand, or tenths of a percent. The IDMS data helped in the estimation of separated isotope aliquot sizes necessary for these "target" ratio values to be created.

Table XVIII describes the aliquotting and coulometric assay data generated. The calibration mixtures 1 through 5 are designated "Cal Mix 1" through "Cal Mix 5" in the Table.

Each calibration mixture was prepared by directly aliquotting portions of the Pu-239 and Pu-242 isotope solutions (denoted as "Pu-239" and "Pu-242", respectively) into a single container, a 30-mL TFE-fluorocarbon bottle, to eliminate the possibility of material losses during transfer and blending operations.

TABLE XVIII
Aliquotting and Coulometric Data
for the Preparation of Calibration Mixtures

Dates of Analyses: 10/2,23,25/84; 11/5,8/84

"Pu-239" Solution			"Pu-242" Solution		
Aliquot No.	Aliquot wt., g	Assay, Pu, mg/g	Aliquot No.	Aliquot wt., g	Assay Pu, mg/g
1	10.58110	0.98038	1	8.28308	1.20387
2	9.82602	0.98006	2	7.56497	1.20339
3	10.23990	0.98017	3	8.37261	1.20441
4	9.68602	0.98040	4	8.83296	1.20380
5	10.66849	0.98001	5	8.19404	1.20383
6	10.68191	0.98067	6	8.81341	1.20310
Cal Mix 1	10.44158	-	Cal Mix 1	8.68231	-
Cal Mix 2	10.00521	-	Cal Mix 2	8.27556	-
Cal Mix 3	9.32683	-	Cal Mix 3	7.68454	-
Cal Mix 4	10.23840	-	Cal Mix 4	8.39198	-
Cal Mix 5	10.06736	-	Cal Mix 5	8.21251	-
7	10.01041	0.98004	7	9.45060	1.20356
8	10.22291	0.97997	8	8.69639	1.20335
9	9.99450	0.98038	9	8.81009	1.20346
10	9.67692	0.98048	10	7.74566	1.20345
11	10.44252	0.98075	11	8.34593	- a
12	9.65255	0.97994	12	8.33236	1.20304
	$\bar{x}$:	0.98027			1.20357
	%RSD:	0.028 (n=12)			0.032 (n=11)

a Outlier.

Table XIX gives quality control information as to the performance of the coulometer making these assay measurements. NBS SRM 949f was used as the standard material. The data list the weight recovery of the plutonium relative to the certified value for each NBS SRM 949f sample analyzed. These quality control standard samples were analyzed concurrently with calibration mixture assay samples, previously described and detailed in Table XVIII.

TABLE XIX

NBS SRM 949f Plutonium Metal Coulometric Assay Data

Dates of analyses: 10/2,23,25/84; 11/5,8/84

Standard No.	Pu, mg taken	Pu, mg found	Relative Difference, %
1925	6.4568	6.4589	+0.032
1922	6.9326	6.9343	+0.024
1921	7.3462	7.3460	-0.002
1924	8.0521	8.0538	+0.021
1928	8.5413	8.5450	+0.044
1929	7.2643	7.2645	+0.002
1930	7.9246	7.9259	+0.016
1943	7.6334	7.6326	-0.011
1946	8.1114	8.1124	+0.012
1947	7.2718	7.2709	-0.012
1948	8.2978	8.2981	+0.004
1949	7.9807	7.9809	+0.002
1952	7.8723	7.8746	+0.029
1955	8.7207	8.7199	-0.009
1350	8.3930	8.3965	+0.042
2657	9.1102	9.1092	-0.011
3030	7.3669	7.3640	-0.039
		$\bar{x}$:	+0.008
		s:	0.022

B. Determination of Pu-242/Pu-239 Ratios of Calibration Mixtures

Table XX gives the Pu-242/Pu-239 ratio of the calibration mixtures determined gravimetrically. The isotope ratio for each calibration mixture was calculated from the isotopic analyses of the separated isotopes and moles of plutonium from each separated isotope determined from the assay and weight of the solution taken. The general equation (1), Section VIII.D., used to calculate the atom ratio of the CRM is applicable to these calculations as well.

Each calibration mixture was thoroughly mixed and gently heated to insure complete homogenization of the isotopes. Each mixture was handled separately to avoid any possibility of cross-

contamination. Finally, aliquots were taken and further diluted with 1 N HNO_3 to a concentration of 33 µg/mL for mass spectrometric analyses.

TABLE XX

Isotopic Composition of Plutonium Calibration Mixtures

Decay-corrected to 10/1/84

Calibration Mixture	Isotope Solution	Solution weight, g*	Pu-239, µmoles	Pu-242, µmoles	Atom Ratio Pu-242/Pu-239
1	"Pu-239"	10.44158	42.7736	0.003890	
	"Pu-242"	8.68231	0.002229	43.1434	1.0086
2	"Pu-239"	10.00521	40.9861	0.003728	
	"Pu-242"	8.27556	0.002125	41.1223	1.0033
3	"Pu-239"	9.32683	38.2071	0.003475	
	"Pu-242"	7.68454	0.001973	38.1854	0.9994
4	"Pu-239"	10.23840	41.9413	0.003815	
	"Pu-242"	8.39198	0.002155	41.7008	0.9942
5	"Pu-239"	10.06736	41.2406	0.003751	
	"Pu-242"	8.21251	0.002109	40.8089	0.9895

*From Table XVIII.

C. Absolute Certification Measurements

Measurements on select CRM units were made using the five calibration mixtures prepared and characterized as described in Sections X.A and X.B. Since the previous provisional certification measurements indicated no sample-to-sample differences between the units, the analysis of only seven units was believed to be adequate for the final certification phase.

Four replicate analyses were made on each of the seven selected CRM units and the five calibration mixtures using the mass spectrometer described in Section III.B.1. A calibration mixture-sample

analytical scheme was employed similar to that shown in Figure 14. To accommodate the analytical scheme, additional measurements were made on two of the calibration mixtures to yield a total of 50 analyses. The sample loading and analytical procedure used for these measurements was identical to that used in the provisional certification measurements. The absolute ratio measurements results are given in Table XXI. The calculated Pu-242/Pu-239 value for NBL CRM 128, corrected for mass fractionation effects, is given in Table XXII. A graphical representation of these results is found in Appendix I.

D. Verification Isotopic Measurements

Verification measurements on aliquots from the CRM units and calibration mixtures were performed at ANL. A Micromass VG-54 thermal ionization mass spectrometer, equipped with a Faraday cup detector, was used for the isotopic analyses.

ANL employed the use of an internal standard while performing the analyses. This technique's description and applications to nuclear safeguards measurements can be found in the literature.[11,12] The internal standard used by ANL was a Pu-240/Pu-244 material. By spiking the samples (CRMs) and calibration mixtures containing Pu-239 and Pu-242 with the internal standard, and by "correcting" these samples' isotope ratios to the internal standard's isotope ratio, a normalized ratio could be calculated which would be applicable to the specific conditions of the analyses. This essentially eliminated run-to-run variations in the ratios and enhanced the external precision of the analyses. Since the calibration mixtures were to be used for the correction factor determination, a well-characterized value for the Pu-240/Pu-244 was not necessary. However, it was necessary to use an identical value for the Pu-240/Pu-244 ratio throughout the analyses so that this normalization would be consistent.

TABLE XXI

Absolute Pu-242/Pu-239 Ratio Measurements
(Certification Measurements)

Decay-corrected to 10/1/84

Calibration Mixture Analyses

Calibration Mixture	Analysis No.	Measured Pu-242/Pu-239	Mean	%RSD	Calculated Pu-242/Pu-239	Correction Factor*
1	1	1.006052				
	2	1.006894				
	3	1.007322				
	4	1.007056	1.006831	0.054	1.008683	1.001839
2	1	1.001090				
	2	1.001161				
	3	1.000688				
	4	1.001574	1.001128	0.036	1.003353	1.002222
3	1	0.997365				
	2	0.996768				
	3	0.997356				
	4	0.996162				
	5	0.997252	0.996981	0.052	0.999469	1.002496
4	1	0.992302				
	2	0.992164				
	3	0.992427				
	4	0.991946	0.992210	0.021	0.994227	1.002038
5	1	0.986652				
	2	0.987690				
	3	0.987064				
	4	0.988024				
	5	0.988007	0.987487	0.061	0.989570	1.002109
					$\bar{x}$:	1.002141
					% RSD:	0.024

*Correction for mass fractionation effects.

TABLE XXI Cont.

NBL CRM 128 Analyses

Unit No.	Analysis No.	Measured Pu-242/Pu-239	Mean	%RSD
001	1	0.998419		
	2	0.998078		
	3	0.999201		
	4	0.999110	0.998702	0.054
144	1	0.997520		
	2	0.997782		
	3	0.998705		
	4	0.998244	0.998063	0.052
287	1	0.998525		
	2	0.998334		
	3	0.998532		
	4	0.998144	0.998384	0.018
498	1	0.998243		
	2	0.998827		
	3	0.997929	0.998333	0.046
724	1	0.998181		
	2	0.997793		
	3	0.999361		
	4	0.999144	0.998620	0.075
855	1	0.997992		
	2	0.998587		
	3	0.997949		
	4	0.997867	0.998099	0.033
996	1	0.998239		
	2	0.998676		
	3	0.998376		
	4	0.998504	0.998449	0.019
		$\bar{x}$:	0.998379	
		%RSD:	0.024	

TABLE XXII

Measured and Corrected Pu-242/Pu-239 Ratio Value for NBL CRM 128 (Certification Measurements)

Decay corrected to 10/1/84

Measured Pu-242/Pu-239 for CRM	Correction Factor from Calibration Mixtures*	Corrected Pu-242/Pu-239 for CRM
0.998379	1.002141	1.000517

*Correction for mass fractionation effects.

Addition of the internal spike to the samples (the CRMs and calibration mixtures) was performed on the sample filament itself. This procedure was used to minimize the consumption of spike and simplify the technique. The relative amount of spike to sample was determined by calculating the ratio of a major isotope in the sample (i.e., Pu-239) to a major isotope in the spike (i.e., Pu-240). This was done to accurately correct for small amounts of Pu-240 found in the samples and small amounts of Pu-239 and Pu-242 in the spike.

To reduce any effect of organic impurities or chemical or isotopic nonequilibration which may exist within the sample-spike mixture, a trace amount of perchloric acid ($HClO_4$) was added to the sample-spike mixture on the filament prior to heating. The heating of the resultant solution to an oxidizing temperature destroyed the $HClO_4$, leaving an equilibrated analyte.

Two replicate analyses were made on each of the CRM samples and calibration mixtures, yielding a total of 24 analyses. The CRM samples and calibration mixtures were run alternately, similar to the analytical scheme shown in Figure 14.

Table XXIII gives the results of ANL's measurements. The calculated Pu-242/Pu-239 value based upon ANL's results and corrected for mass fractionation effects is given in Table XXIV.

TABLE XXIII

ANL Absolute Pu-242/Pu-239 Ratio Measurements (Verification Measurements)

Decay-corrected to 10/1/84

Calibration Mixtures Analyses

Calibration Mixture	Measured Pu-242/Pu-239	Calculated Pu-242/Pu-239	Correction Factor*
1	1.00711	1.008683	1.00156
2	1.00185	1.003353	1.00150
3	0.99791	0.999469	1.00156
4	0.99262	0.994301	1.00169
5	0.98793	0.989570	1.00166
		$\bar{x}$:	1.00159
		% RSD:	0.008

CRM 128 Analyses

Unit No.	Measured Pu-242/Pu-239
001	0.99922
144	0.99915
287	0.99925
498	0.99913
724	0.99912
855	0.99930
996	0.99923
$\bar{x}$:	0.99920
% RSD:	0.007

*Correction for mass fractionation effects.

TABLE XXIV

Measured and Corrected Pu-242/Pu-239 Values for NBL CRM 128 (ANL Verification Measurements)

Decay corrected to 10/1/84

Measured Pu-242/Pu-239 for CRM	Correction Factor from Calibration Mixtures*	Corrected Pu-242/Pu-239
0.99920	1.00159	1.00079

*Correction for mass fractionation effects.

XI. STATISTICAL EVALUATION

A. Preliminary Discussion

A thorough statistical evaluation of the CRM's Pu-242/Pu-239 isotopic ratio required an exhaustive and rigorous assessment of each individual component, or factor, used to calculate the ratio. These factors are incorporated into equation (1) used to calculate the ratio from the isotopic composition of the separated isotopes and moles of plutonium from each separated isotope solution. These same factors are used to determine the isotope ratio values for the calibration mixtures used to bias-correct the mass spectrometry data.

In generating the uncertainty of the CRM's certified value, it is necessary to consider the uncertainties associated with each factor. These uncertainties reflect the systematic and random errors of the coulometric, weighing, and mass spectrometric measurement systems. Therefore, the calculation of the absolute ratio value using the coulometric data has an uncertainty solely determined from these factors. The calculation of the absolute ratio value using the mass spectrometric data has an uncertainty factor due to the calibration mixtures analyzed, as well as the errors associated with the mass spectrometry measurements of the CRM itself.

A relationship can be established between the factors used to calculate the certified value since each factor, although independently determined, is needed to perform the final ratio calculation.

B. Theory (Derivation of Formulas)

The following explanations and assumptions are the theoretical basis for calculating the uncertainty of the CRM's certified value, based upon multivariate analysis.

Arbitrary variables, such as X_1, X_2,...X_n, can be used to represent factors in a first-order (linear) combination. In strict mathematical terms, a linear combination of these variables can be expressed as:

$$\sum_{i=1}^{n} A_i * X_i \quad , \tag{4}$$

where the A_i's are constants.

From multivariate calculus it may be shown that an arbitrary function (F) of variables X_1, X_2,...X_n can be approximated as:

$$\sum_{i=1}^{n} \frac{\partial F}{\partial X_i} * X_i + K \quad , \tag{5}$$

where: $\frac{\partial F}{\partial X_i}$ = the partial derivative of F with respect to X_i, and

K = a constant.[13]

This can be related to the determination of standard errors for each uncertainty component.

Given a set of parameters X_1, X_2,...X_n, and a set of corresponding independent estimates X_1, X_2,...X_n with corresponding standard errors $S(X_1)$, $S(X_2)$,...$S(X_n)$, having

corresponding degrees of freedom $df(S(X_1))$, $df(S(X_2))$, ...$df(S(X_n))$, a linear combination, C, of these quantities can be expressed as:

$$C = \sum_{i=1}^{n} A_i * X_i \tag{6}$$

where the A_i's are constants.

The standard error of C, expressed as S(C), can be calculated by

$$S(C)^2 = \sum_{i=1}^{n} A_i^2 * S(X_i)^2 \tag{7}$$

and the degrees of freedom for S(C), expressed as df(S(C)), are approximated by

$$df(S(C)) = \frac{\left[\sum_{i=1}^{n} A_i^2 * S(X_i)^2\right]^2}{\left[\sum_{i=1}^{n} \frac{A_i^4 * S(X_i)^4}{df(X_i)}\right]} \tag{8}$$

Equation (8) is known as Satterthwaite's Approximation.[14,15]

From equations (7) and (8) it can be concluded that for most functions F of a set of estimates X_1, X_2,...X_n, the standard error of F, expressed as S(F), can be approximated by:

$$S(F)^2 = \sum_{i=1}^{n} \left(\frac{\partial F}{\partial X_i}\right)^2 * S(X_i)^2, \tag{9}$$

with degrees of freedom for S(F), df(S(F)),[16] being approximated as:

$$df(S(F)) = \frac{\left[\sum_{i=1}^{n} \left(\frac{\partial F}{\partial X_i}\right)^2 * S(X_i)^2\right]^2}{\left[\sum_{i=1}^{n} \frac{\left(\frac{\partial F}{\partial X_i}\right)^4 * S(X_i)^4}{df(X_i)}\right]} \tag{10}$$

The standard error of the product of two independent quantity estimates A and B, S(A*B), with standard errors of S(A) and S(B), respectively, can be calculated using the following formula:

$$S(A * B)^2 = [A * S(B)]^2 + [B * S(A)]^2 + [S(A) * S(B)]^2 \quad (11)$$

The third term in equation (11) is negligible in practice, but is included in the calculation. The degrees of freedom for the standard error S(A*B), symbolized as df(S(A*B), can be obtained similarly using only the first two terms of equation (11) and the degrees of freedom of the quantities S(A) and S(B), df(S(A)) and df(S(B)), respectively:

$$df(S(A*B)) = \frac{[(A * S(B))^2 + (B * S(A))^2]^2}{\frac{(A * S(B))^4}{df(S(B))} + \frac{(B * S(A))^4}{df(S(A))}} \quad (12)$$

The 95% confidence interval of a quantity estimate X, denoted as C.I.(X), with a standard error of S(X) with df(S(X)) degrees of freedom, is calculated using the following formula:

$$C.I.(X) = X \pm t[95\%, df(S(X))] * S(X) \quad (13)$$

where t[95%, df(S(X))] represents the two-sided Student's "t" value at the 95% confidence level with df(S(X)) degrees of freedom and X - t[95%, df(S(X))] * S(X) and X + t[95%, df(S(X))] * S(X) are understood to be the lower and upper limits of the interval respectively.[17]

C. Calculation of the NBL CRM 128 Certified Value and Associated Uncertainty

1. Controlled-Potential Coulometric Value

Table XXV defines the variables, in descriptive and numerical terms, which are used to calculate the Pu-242/Pu-239 ratio as determined by coulometry (R_c) using the formula:

$$R_C = \frac{(X_1 * X_2 * X_3) + (X_4 * X_5 * X_6)}{(X_1 * X_2 * X_7) + (X_4 * X_5 * X_8)} * M \qquad (14)$$

where 239.05216 and 242.05874 are the nuclide masses of Pu-239 and Pu-242 used to calculate M (see Appendix II).

TABLE XXV

Variables Used in the Calculation of the NBL CRM 128 Absolute Pu-242/Pu-239 Value Based Upon Coulometry

Variable	Description	Value	Error	df
X_1	Weight of Solution "242", g	383.3478	0.0001	-
X_2	Pu concentration of "242", mg Pu/g soln.	1.45441	0.00004	3
X_3	Pu-242 abundance in "242", weight percent	99.9376	0.0011	5
X_4	Weight of Solution "239", g	384.1705	0.0001	-
X_5	Pu concentration of "239", mg Pu/g soln.	1.43285	0.00007	3
X_6	Pu-242 abundance in "239", weight percent	0.0092	0.00019	5
X_7	Pu-239 abundance in "242", weight percent	0.0051	0.0002	5
X_8	Pu-239 abundance in "239", weight percent	99.8978	0.00019	5
M	Ratio, nuclide mass of Pu-239/nuclide mass of Pu-242	0.98758	-	-

The following formula can be used to calculate R_C's uncertainty (as standard error):

$$S(R_C)^2 = \sum_{i=1}^{8} \left(\frac{\partial R_C}{\partial X_i}\right)^2 * S(X_i)^2 \qquad (15)$$

where: $\frac{\delta R_C}{\delta X_i}$ represents the partial derivative of R_C with respect to X_i. An example of such a partial derivative determination is given in equation (16).

$$\frac{\partial R_C}{\partial X_1} = \frac{(X_2 * X_4 * X_5 * X_8) * (X_3 - X_7)}{[(X_1 * X_2 * X_7) + (X_4 * X_5 * X_8)]^2} * M \qquad (16)$$

Satterthwaite's approximation, as applied to $df(S(R_C))$, is:

$$df(S(R_C)) = \frac{\left[\sum_{i=1}^{8} \left(\frac{\partial R_C}{\partial X_i}\right)^2 * S(X_i)^2\right]^2}{\left[\sum_{i=1}^{8} \frac{\left(\frac{\partial R_C}{\partial X_i}\right)^4 * S(X_i)^4}{df(X_i)}\right]} \qquad (17)$$

Using equations (14), (15), and (17), the calculated Pu-242/Pu-239 value, as determined by coulometry, and decay-corrected to 10/1/84 is 1.00073, with a standard error of 0.00006 (df = 5).

2. Mass Spectrometric Value

The following equation was used to calculate the bias-corrected Pu-242/Pu-239 ratio as determined by mass spectrometry, R_M:

$$R_M = CF_{\bar{X}} * R_{u,\bar{X}}, \qquad (18)$$

where: $CF_{\bar{X}}$ = the mean of the correction factor as determined by mass spectrometry using calibration mixtures, and

$R_{u,\bar{x}}$ = the mean of the uncorrected Pu-242/Pu-239 ratios of NBL CRM 128 as determined by mass spectrometry.

The correction factor ($CF_{\bar{x}}$) is calculated using the following equation:

$$CF_{\bar{x}} = \frac{1}{5} * \sum_{i=1}^{5} \frac{R_{t,i}}{R_{u,i}} \qquad (19)$$

where: $R_{t,i}$ = the theoretical (or calculated) Pu-242/Pu-239 ratio of calibration mixture i (Table XX), and

$R_{u,i}$ = the uncorrected Pu-242/Pu-239 ratio of calibration mixture i, as determined by mass spectrometry.

The formula given in equation (19) is used to calculate the theoretical Pu-242/Pu-239 ratio of each calibration mixture i ($R_{t,i}$):

$$R_{t,i} = \frac{(a_1 * A * X_{1,i}) + (b_1 * B * X_{2,i})}{(a_2 * A * X_{1,i}) + (b_2 * B * X_{2,i})} * M \qquad (20)$$

Table XXVI defines the variables, in descriptive and numerical terms, which were used to calculate the $R_{t,i}$ of each calibration mixture. Table XXVII gives the $X_{1,i}$ and $X_{2,i}$ values as well as the calculated $R_{t,i}$ value for each calibration mixture. Table XXVIII gives the value for $R_{u,i}$ and the correction factor CF_i for each calibration mixture i as calculated using the mathematical relationship defined in equation (19).

TABLE XXVI

Variables Used in the Calculation of the Pu-242/Pu-239 Value for the Calibration Mixtures

Variable	Description	Value	Error	df
a_1	Pu-242 abundance in "239", weight percent	0.0092	0.00019	5
b_1	Pu-242 abundance in "242", weight percent	99.9376	0.0011	5
a_2	Pu-239 abundance in "239", weight percent	99.8978	0.00019	5
b_2	Pu-239 abundance in "242", weight percent	0.0051	0.0002	5
A	Pu concentration of "239", mg Pu/g soln.	0.98027	0.00081	11
B	Pu concentration of "242", mg Pu/g soln.	1.20357	0.00118	10
$X_{1,i}$	Grams "239" solution in i^{th} calibration soln.	See Table XXVII	-	-
$X_{2,i}$	Grams "242" solution in i^{th} calibration soln.	See Table XXVII	-	-

TABLE XXVII

Values of $X_{1,i}$, $X_{2,i}$, and $R_{t,i}$ for Calibration Mixtures "i"

i	$X_{1,i}$*	$X_{2,i}$*	$R_{t,i}$**
1	10.44158	8.68231	1.0086
2	10.00521	8.27556	1.0033
3	9.32683	7.68454	0.9994
4	10.23840	8.39198	0.9942
5	10.06736	8.21251	0.9895

* From Tables XVIII and XX.
** From Table XX.

TABLE XXVIII

Values of $R_{u,i}$ and Calculated Correction Factor CF_i for Each Calibration Mixture "i"

i	$R_{u,i}$	Standard Error for $R_{u,i}$	$R_{t,i}$	df	CF_i
1	1.0068	0.00024	1.0086	3	1.0018
2	1.0011	0.00018	1.0033	3	1.0022
3	0.9970	0.00023	0.9994	4	1.0024
4	0.9922	0.00010	0.9942	3	1.0020
5	0.9875	0.00028	0.9895	4	1.0020
					$\bar{x}$: 1.0021

In order to determine the standard error of the mass spectrometric measurements, equations (19) and (20) were combined to yield equation (21):

$$CF_{\bar{x}} = \sum_{i=1}^{5} \frac{M * [(a_1 * A * X_{1,i}) + (b_1 * B * X_{2,i})]}{5 * R_{u,i} * [(a_2 * A * X_{1,i}) + (b_2 * B * X_{2,i})]} \qquad (21)$$

where a_1, b_1, a_2, b_2, $X_{1,i}$, $X_{2,i}$, and M are considered to have negligible uncertainties. A, B, and $R_{u,i}$ are considered to have non-negligible uncertainties.

Since A and B appear in all terms in equation (21), the formula used to calculate the standard error of $CF_{\bar{x}}$, expressed as $S(CF_{\bar{x}})$ is:

$$S(CF_{\bar{x}})^2 = \sum_{i=1}^{5} \left[\frac{\partial CF_{\bar{x}}}{\partial R_{u,i}} * S(R_{u,i})\right]^2 + \left[\frac{\partial CF_{\bar{x}}}{\partial A} * S(A)\right]^2 + \left[\frac{\partial CF_{\bar{x}}}{\partial B} * S(B)\right]^2 \qquad (22)$$

with degrees of freedom, expressed as $df(S(CF_{x}-))$, given by:

$$df(S(CF_{\bar{x}})) = \frac{\left\{ \sum_{i=1}^{5} \left[\frac{\partial CF_{\bar{x}}}{\partial R_{u,i}} * S(R_{u,i}) \right]^2 + \left[\frac{\partial CF_{\bar{x}}}{\partial A} * S(A) \right]^2 + \left[\frac{\partial CF_{\bar{x}}}{\partial B} * S(B) \right]^2 \right\}^2}{\sum_{i=1}^{5} \frac{\left[\frac{\partial CF_{\bar{x}}}{\partial R_{u,i}} * S(R_{u,i}) \right]^4}{df(S(R_{u,i}))} + \frac{\left[\frac{\partial CF_{\bar{x}}}{\partial A} * S(A) \right]^4}{df(S(A))} + \frac{\left[\frac{\partial CF_{\bar{x}}}{\partial B} * S(B) \right]^4}{df(S(B))}} \quad (23)$$

Using equations (18), (19), (22) and (23), the mass spectrometrically-determined Pu-242/Pu-239 ratio value using the correction factors calculated from calibration mixtures (1.00216) applied to an uncorrected NBL CRM 128 Pu-242/Pu-239 value of 0.99837 ($R_{u,\bar{x}}$), is 1.00052, with a standard error of 0.00020 (df=19), decay-corrected to 10/1/84.

D. NBL CRM 128 Certified Value and Associated Uncertainty

The unweighted mean of the coulometric and mass spectrometric Pu-242/Pu-239 values was determined and established as the certified value for NBL CRM 128. Table XXIX summarizes the values and uncertainties used to derive the certified value (R_{cert}).

TABLE XXIX

NBL CRM 128 Certified Pu-242/Pu-239 Value Calculation

Decay-corrected to 10/1/84

Quantity	Value	Standard Error	df
Pu-242/Pu-239 as calculated from coulometry (R_C)	1.00073	0.00006	5
Pu-242/Pu-239 as calculated from mass spectrometry (R_M)	1.00052	0.00020	19
Combined unweighted mean (R_{cert})	1.00063	0.00013	21

The standard error and degrees of freedom were determined based upon the fact that R_{cert} is calculated by:

$$R_{cert} = (R_C + R_M) * 0.5 \qquad (24)$$

making R_{cert} not only the mean of R_M and R_C, but a linear combination of the two determinations. Consequently, the standard error of R_{cert} is calculated as:

$$S(R_{cert})^2 = [S(R_C)^2 + S(R_M)^2] * 0.25 \qquad (25)$$

having degrees of freedom calculated as:

$$df(S(R_{cert})) = \frac{\left[(0.5 * S(R_C))^2 + (0.5 * S(R_M))^2\right]^2}{\frac{(0.5 * S(R_C))^4}{df(S(R_C))} + \frac{(0.5 * S(R_M))^4}{df(S(R_M))}} \qquad (26)$$

Based upon t[95%, 21] = 2.08, the 95% confidence interval for R_{cert} using equation (13) is 1.00063 ± 0.00026.

E. Isotopic Abundance Values for NBL CRM 128 Based Upon Absolute Certification Measurements

Table XXX gives the isotopic distribution of the CRM as calculated using minor isotope ratio data generated during the provisional certification work (Section IX.), but normalized to the absolute Pu-242/Pu-239 ratio of 1.00063. As can be observed by comparing the isotopic data in Table XXX with the isotopic data in Table XVII, no change in the minor isotopic distribution was observed in the significant figures given due to the small (0.07%) difference between the provisional and absolute certified Pu-242/Pu-239 ratio values. These minor isotope abundance values are given for information purposes only and are not certified.

TABLE XXX

Isotopic Distribution of NBL CRM 128
(Absolute Certification Measurements)

Decay-corrected to 10/1/84

Isotope	Atom %
Pu-238	0.004
Pu-239	49.928
Pu-240	0.035
Pu-241	0.036
Pu-242	49.997
Pu-244	<0.001

XII. DISCUSSION

The results from the two sets of measurements made by NBL and one set by ANL provide absolute isotopic ratio data for NBL CRM 128. The summary of these measurements is shown in Table XXXI.

The overall spread of the three sets of data was observed to be 0.00027, with each of the mass spectrometry sets bracketing the certified value (1.00063). Although the certified value's uncertainty (±0.00026) includes all three sets of data (graphically shown in Figure 15, Appendix I), the relatively large spread between NBL's and ANL's mass spectrometry measurements required further study.

TABLE XXXI

Summary of Absolute Pu-242/Pu-239 Ratio Measurements

Decay-corrected to 10/1/84

Laboratory	Method	Pu-242/Pu-239 Ratio	Standard Error
NBL	Coulometry (mass)	1.00073	0.00006
NBL	Mass Spectrometry	1.00052	0.00020
ANL	Mass Spectrometry	1.00079	0.00005

An experiment was performed involving the analysis of calibration mixtures and CRM samples using direct additions of $HClO_4$ to the sample filament. This study was to determine if the cause of the spread between the mass spectrometry data sets was due to ANL's addition of $HClO_4$ to their samples prior to analysis, as no $HClO_4$ was added to NBL's samples. By comparing these isotopic results to the certification measurements not involving $HClO_4$, a bias in the ratio due to any chemical effect of $HClO_4$ should be evident.

Isotopic measurements on five CRM units and the five calibration mixtures were made. A single drop of a 10% $HClO_4$ solution, with a volume of approximately one µL was added to 100 ng of plutonium deposited onto a single sample filament. The solution was evaporated and oxidized. This oxidation should have driven off the $HClO_4$, as evidenced by the white vapor emanating from the filament during the high temperature heating. The results of these measurements are given in Table XXXII.

TABLE XXXII

Absolute Pu-242/Pu-239 Ratio Measurements of Samples Treated with Perchloric Acid

Decay-corrected to 10/1/84

Calibration Mixtures Analyses

Calibration Mixture	Calculated Ratio	Measured Ratio	Mean Measured Ratio	Correction Factor
1	1.0086	1.007627		
		1.007047	1.007337	1.0013
2	1.0033	1.002290		
		1.002605	1.002448	1.0008
3	0.9994	0.998462		
		0.997724	0.998093	1.0013
4	0.9942	0.993615		
		0.993329	0.993472	1.0007
5	0.9895	0.988193		
		0.988244	0.988219	1.0013
			$\bar{x}$:	1.0011
			%RSD:	0.030

TABLE XXXII (Cont.)

CRM 128 Analyses

Unit No.	Measured Ratio	Mean Measured Ratio	Corrected Ratio
498	0.999537		
	0.999000	0.999269	1.0004
724	1.000352		
	0.999807	1.000080	1.0012[a]
287	0.999029		
	0.999653	0.999341	1.0004
996	0.999620		
	0.999410	0.999515	1.0006
001	0.999012		
	0.999368	0.999190	1.0003
		$\bar{x}$:	1.0004
		%RSD:	0.013

Percent Relative Difference from original NBL Mass Spectrometry Value: -0.001

[a] Outlier; possibly due to a solution concentration problem.

The results of this experiment suggested that the $HClO_4$ addition did not have any effect on the physicochemical properties of the sample while undergoing thermal ionization in the mass spectrometer. This information further supports the rigorousness of the equilibration performed on the CRM material and calibration mixtures. Apparently, the "bias", if it does exist at all, lies elsewhere in the ratio determination process when using the internal standard technique.

XIII. CONCLUSION

The certification and issuance of NBL CRM 128 on an absolute basis makes available, for the first time, a plutonium isotopic standard certified relative to the isotopic vaporization and ionization behavior of plutonium. The use of the standard for isotopic measurements on plutonium materials allows for direct traceability between IDMS and wet chemical measurements (such as coulometric

assay) routinely performed for safeguards accountability. The availability of the CRM to the international nuclear communities places their mass spectrometric measurements of plutonium on an absolute basis and establishes compatibility with the U.S. measurements base.

The importance of this reference material has been recognized by the U.S. DOE and its contractors not only for providing traceable measurements, but also in its use as an accurate reference point for domestic measurement evaluation programs. The Safeguards Measurement Evaluation Program, administered by NBL, is committed to the use of the CRM as the reference base for all plutonium isotopic characterization work in the Program. Also, EG&G's Rocky Flats Plant, administrator of the Plutonium Isotope Exchange Program, has agreed that all isotope exchange sample data should be normalized to the NBL CRM 128 reference base.

NBL CRM 128 will be the basis of further improvements in the area of plutonium isotopic and assay measurement methods and reference materials. This project has generated a large body of data in order to perform meaningful comparisons between both internal and external normalization and corrections for isotope ratio measurements. Because the use of the CRM establishes plutonium IDMS and other plutonium assay techniques on an absolute basis, continued development and more extensive use of IDMS as an accurate verification and certification method for use in plutonium assay is anticipated.

Prior to the issuance of NBL CRM 128, available plutonium isotopic standards had certified values which, in most cases, were not representative of state-of-the-practice measurements in mass spectrometry. The quality of the characterization effort on this CRM has resulted in an isotopic standard which is certified to the limits of research-quality, state-of-the-art instrumentation. This

CRM will serve as the calibration base for a planned new series of plutonium isotopic standards which will serve the expanding needs of the nuclear research and safeguards communities.

The following information is in the Appendices: Appendix I contains graphical representations of the absolute measurements data by mass spectrometry. Appendix II contains the physical constants used in the calculation of isotope ratios and their decay-corrected values and Faraday's constant used in the coulometric calculations. Appendix III contains the NBL CRM 128 certificates of analysis based upon the provisional certification measurements and the absolute certificatior measurements, as well as certificates of analysis for NBS SRM 949f and NBS SRM 947. Also found in Appendix III is a photograph of a NBL CRM 128 unit (Figure 19) showing the DOE and U.S. Department of Transportation (DOT) approved shipping containers for the distribution of the CRM from NBL to its users.

Finally, Annex I compares isotopic fractionation behavior of uranium and plutonium while undergoing thermal ionization, using information and data obtained from different experiments performed in the development work described in this report.

APPENDIX 1

Graphical Representation of the Absolute Measurements Data

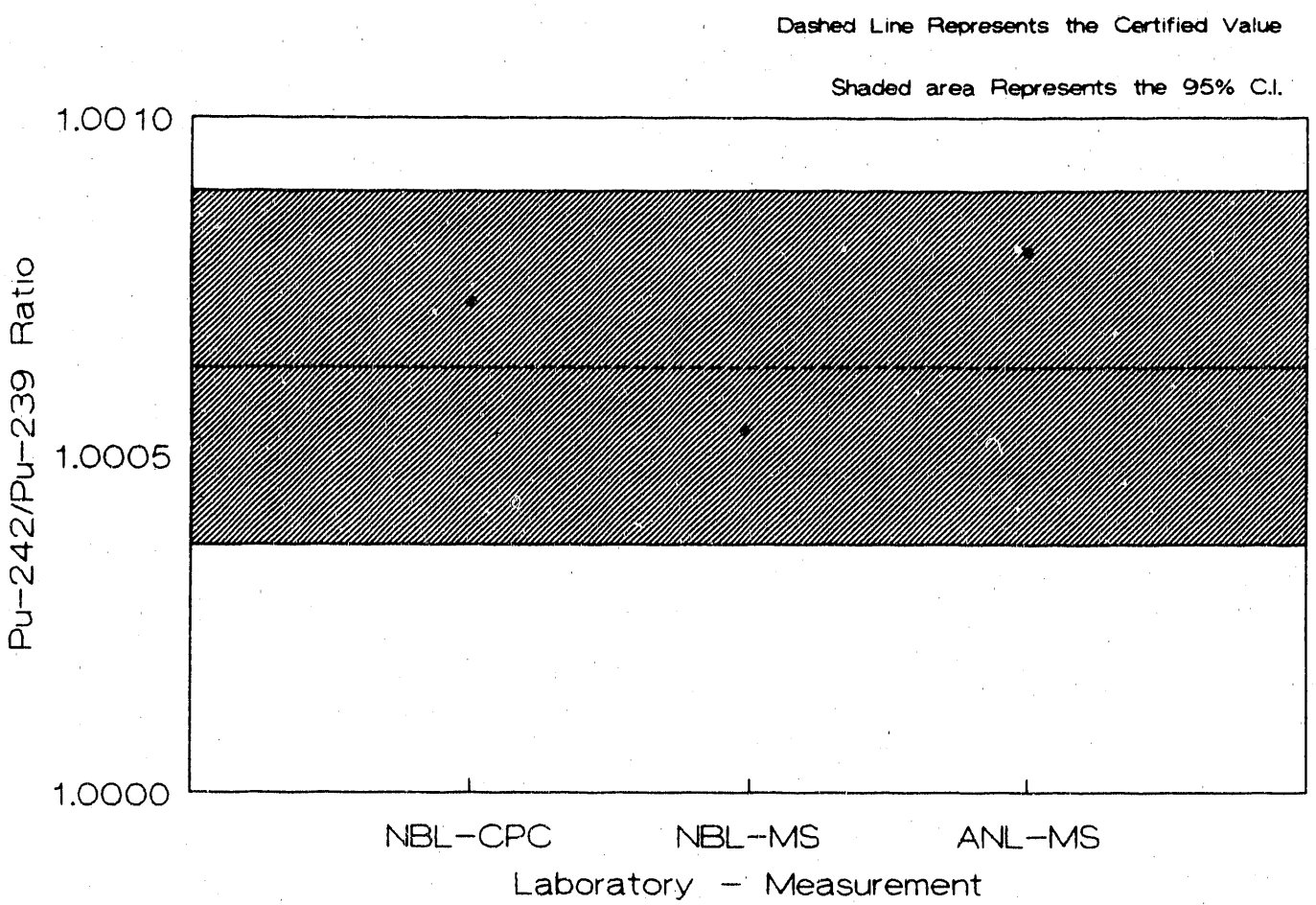

Figure 15. Absolute Pu-242/Pu-239 Ratio Data

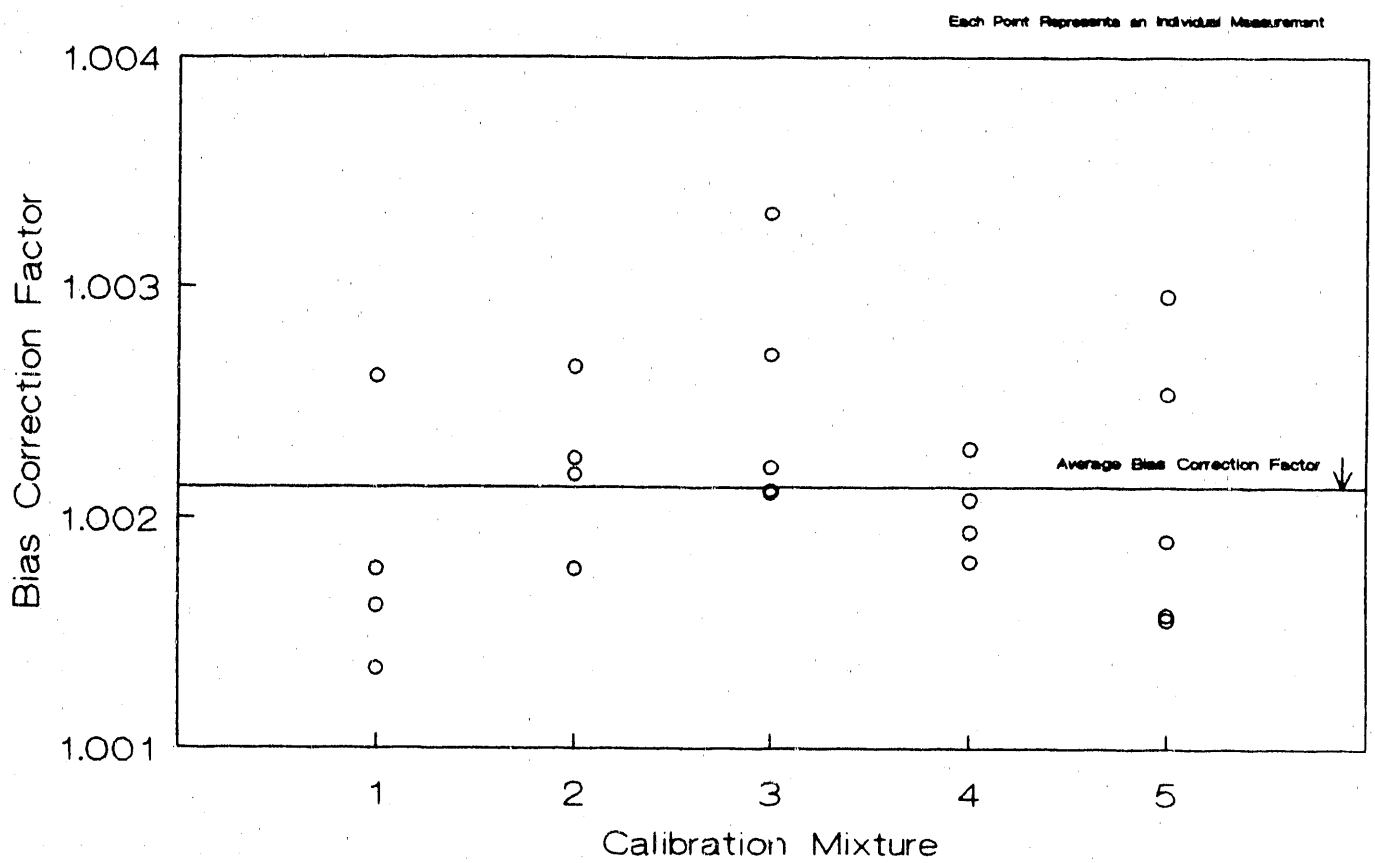

Figure 16. Reproducibility of Pu-242/Pu-239 Bias Correction Within Calibration Mixtures Analyses (Certification Measurements)

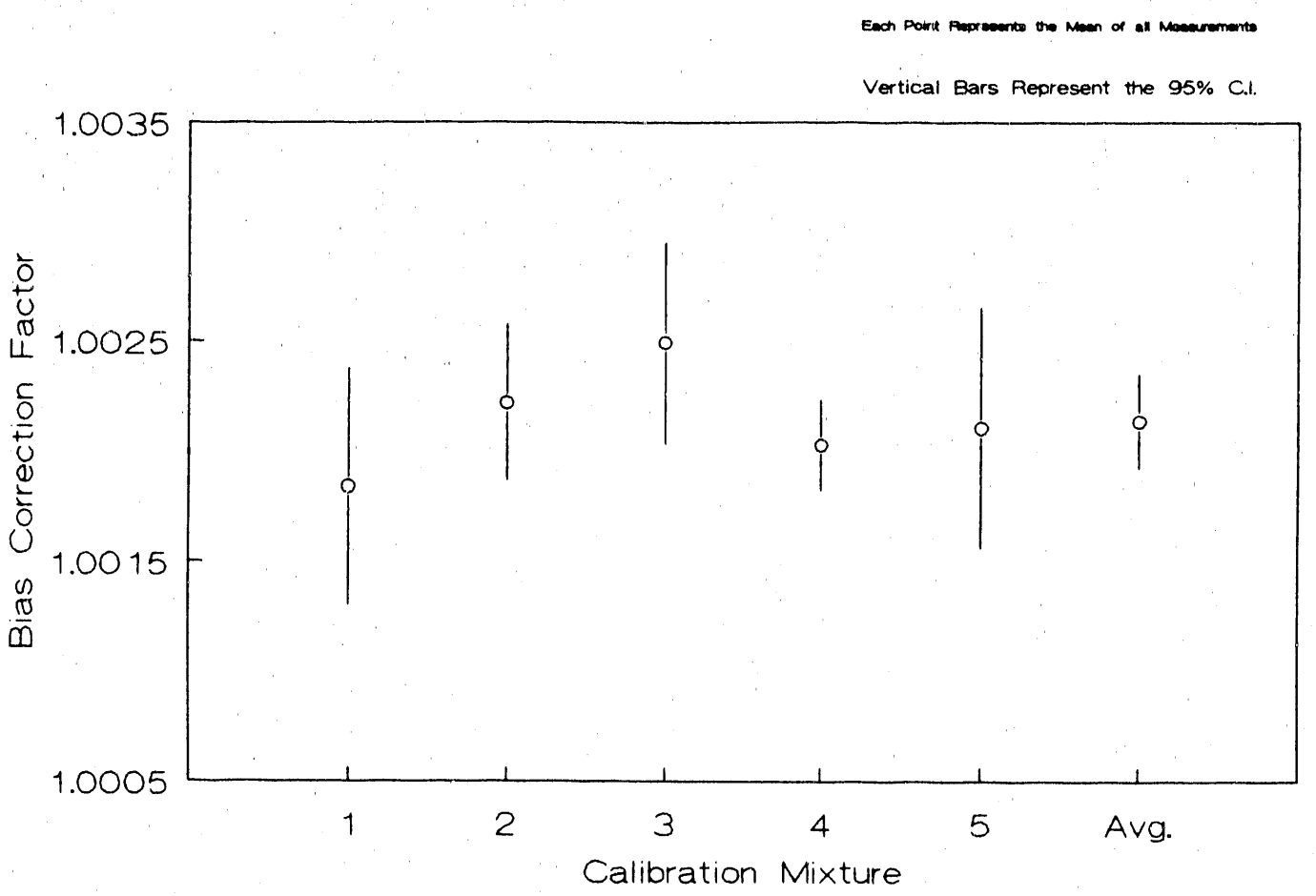

Figure 17. Calibration Mixture vs. Bias Correction Value
(Certification Measurements)

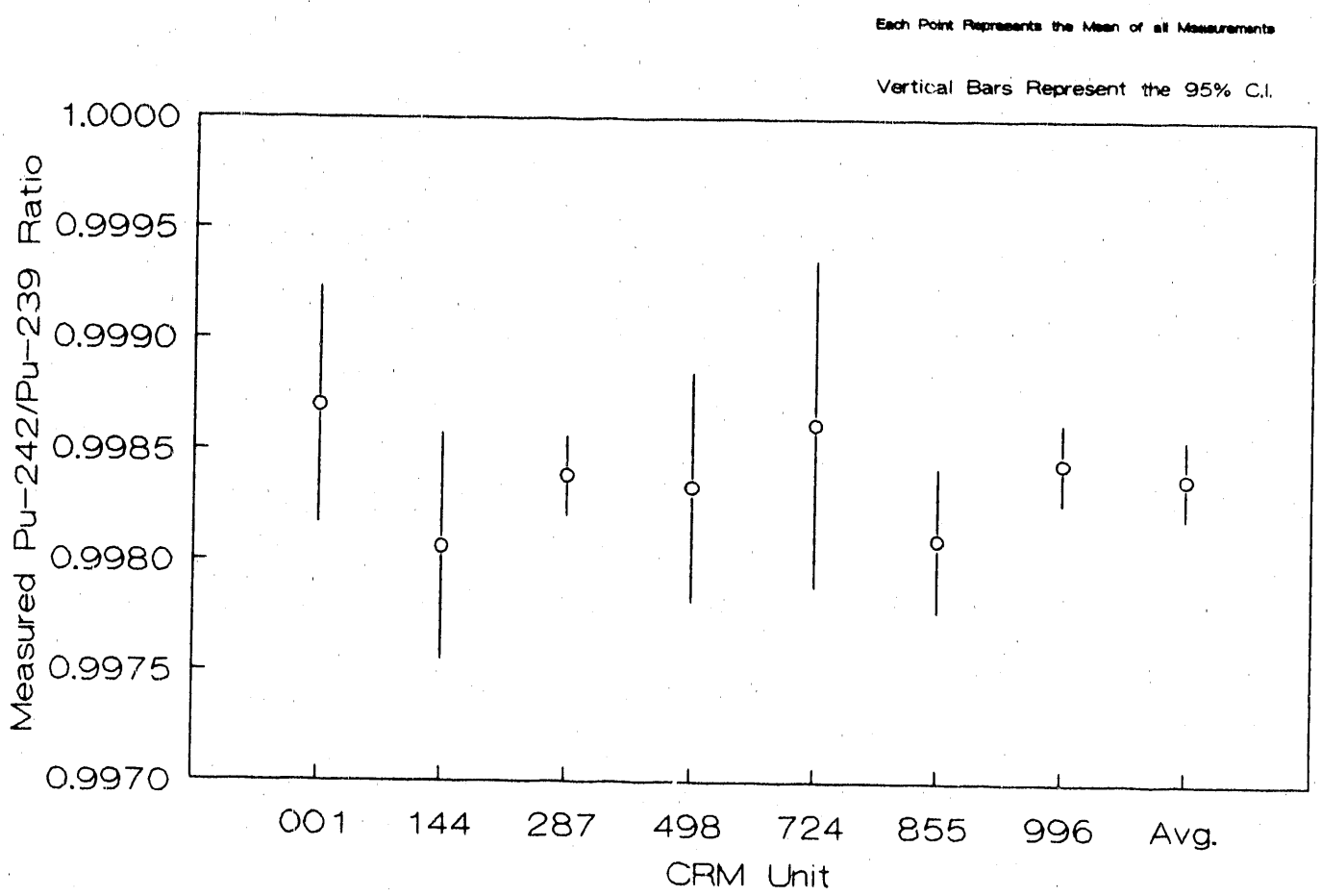

Figure 18. CRM Unit Number vs. Measured Pu-242/Pu-239 Ratio (Certification Measurements)

APPENDIX II

Physical Contants Used in Calculations

Plutonium

Nuclide masses[18] and Half-lives*

Isotope	Nuclide Mass	Half-lives in years
238	238.04956	87.74
239	239.05216	24119
240	240.05381	6562
241	241.05685	14.35
242	242.05874	376000
244	244.06420	$\sim 8 \cdot 10^7$

Faraday constant = $9.64856 \cdot 10^4$ coulombs/mole

*DOE Half-life Committee

APPENDIX III

Certificates of Analysis

U. S. Department of Energy
New Brunswick Laboratory

New Brunswick Laboratory Certified Reference Materials Provisional Certificate of Analysis

CRM No. 128

Plutonium-239/Plutonium-242, 1:1 Atom Ratio In Nitrate Form (Plutonium Isotopic Standard)

(In cooperation with the U. S. Department of Commerce, National Bureau of Standards, Gaithersburg, Maryland)

Plutonium-239/Plutonium-242 . . . . . $0.99862_0 \pm 0.00061_1$ Atom Ratio*

*As of July 1, 1984. Refer to Table I for Yearly Decay-Adjusted Values

This Certified Reference Material (CRM) is primarily intended for the calibration of mass spectrometers used to perform plutonium isotopic measurements. The specific purpose of this isotope standard is for the determination of a mass discrimination factor which will place measured plutonium isotopic ratios on an absolute basis. Each unit of CRM No. 128 consists of approximately 1 mg of a nominal 1:1 mixture of ^{239}Pu and ^{242}Pu, as evaporated plutonium nitrate contained in a 30-mL Teflon bottle.

CRM No. 128 is available at this time on PROVISIONAL CERTIFICATION ONLY. The ratio herein supplied is corrected for mass discrimination effects *relative to* the $^{239}Pu/^{240}Pu$ ratio of NBS SRM 947. Final certification of the CRM to establish the absolute ratio will not, however, involve use of this SRM; rather it will be based solely on isotopic ratio measurements of specially prepared $^{239}Pu/^{242}Pu$ calibration mixtures.

The statistical uncertainty assigned to the provisionally certified value is an approximate 95% confidence interval for the unweighted mean. The uncertainty takes into account random measurement variations, the uncertainty of the mass discrimination correction extrapolated from the $^{239}Pu/^{240}Pu$ ratio of the NBS SRM 947, and the known reproducibility of the mass spectrometer used to perform the measurements.

The plutonium materials used to produce this CRM were obtained from the ORNL Isotope Sales Group with the approval of the DOE Research Materials/Transplutonium Program Committee chaired by J. L. Burnett. Preparation and assay measurements of the isotope mixture were performed by C. G. Cacic, NBL; isotopic measurements were performed by D. W. Crawford, NBL; impurity measurements were performed by J. A. Carter and associates, ORNL. Technical assistance was provided by L. A. Machlan, National Bureau of Standards (NBS). Statistical assessment of the data for provisional certification was performed by J. T. Bracey and M. D. Soriano, NBL. Initial project technical direction was provided by E. L. Garner, NBS; overall direction and coordination of the preparation, provisional certification and issuance of this CRM were provided by N. M. Trahey, NBL.

October 1, 1984
Argonne, Illinois

Carleton D. Bingham
Director

(Over)

The plutonium isotopes (≥99.9% isotopic purity) comprising CRM No. 128 were separately dissolved, chemically purified and assayed by controlled potential coulometry before being combined by weight, isotopically equilibrated, apportioned and dried into units. Isotopic characterization and certification measurements were performed on CRM units randomly selected according to a statistical sampling plan, then dissolved and subsampled. The $^{239}Pu/^{242}Pu$ ratio of each subsample was determined by thermal ionization mass spectrometry. Total elemental impurity content was determined by spark source mass spectrometry on selected subsamples and is estimated to be 300 μg/g plutonium. Although the CRM was americium-free at the time of preparation, the calculated americium ingrowth from the decay of ^{241}Pu present in small amounts in the CRM is 16 μg/g plutonium as of July 1, 1984, and will increase at a rate of approximately 18 μg/g plutonium per year.

CRM No. 128 had a radioactivity of 2.7×10^6 Bq (73 μCi) per unit as of July 1, 1984, which is dominated by ^{239}Pu and ^{241}Pu.

The change with time in the CRM No. 128 certified ratio is very small, due to the relatively long half-lives of the primary plutonium isotopes. Table I provides decay-adjusted values for the certified ratio at one-year intervals for a five-year period.

TABLE I

CRM No. 128 Yearly Decay-Adjusted Atom Ratio Value

July 1, 1985	July 1, 1986	July 1, 1987	July 1, 1988	July 1, 1989
0.99859_3	0.99856_6	0.99853_9	0.99851_3	0.99848_6

The plutonium isotopic distribution of CRM No. 128 is given in Table II and is for informational purposes only (not certified).

TABLE II

CRM No. 128 Isotopic Distribution (as of July 1, 1984)

Plutonium Isotope:	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{244}Pu
Atom Percent:	0.004	49.928	0.035	0.036	49.997	<0.001

(The half-life values used to calculate the values in Tables I and II are expressed in years: ^{238}Pu — 87.74; ^{239}Pu — 24,119; ^{240}Pu — 6,540; ^{241}Pu — 14.35; ^{242}Pu — 376,000.)

RECOMMENDED PROCEDURE FOR USING CRM NO. 128

Each CRM unit contains 1 ± 0.03 mg of material and is designed for *in-situ* dissolution. When converted to solution form, a unit can be used as is. No additional purification of the CRM is required.

Wipe the Teflon bottle with a chamois or damp cloth to dissipate any static charge which may cause expulsion of the material upon opening. Unscrew the cap, add 1N HNO_3 to the CRM concentration desired and carefully warm the bottle to insure total dissolution. *Do not heat the bottle above 150°C because bottle deformation will occur!* Replace and tighten the cap, then allow the bottle to cool before shaking to homogenize contents. Wipe cap and bottle threads each time a portion of the CRM solution is removed from the bottle.

U. S. Department of Energy
New Brunswick Laboratory

New Brunswick Laboratory Certified Reference Materials Certificate of Analysis

CRM No. 128

Plutonium-239/Plutonium-242, 1:1 Atom Ratio In Nitrate Form (Plutonium Isotopic Standard)

Plutonium-239/Plutonium-242 ..... $0.9993_7 \pm 0.0002_6$ Atom Ratio*

*As of October 1, 1984. Refer to Table I for Yearly Decay-Adjusted Values

This Certified Reference Material (CRM) is primarily intended for the calibration of mass spectrometers used to perform plutonium isotopic measurements. The specific purpose of this isotope standard is for the determination of a mass discrimination factor which will place measured plutonium isotopic ratios on an absolute basis. Each unit of CRM No. 128 consists of approximately 1 mg of a nominal 1:1 mixture of ^{239}Pu and ^{242}Pu, as evaporated plutonium nitrate contained in a 30-mL Teflon bottle. *NOTE: The bottle and its outer plastic containment should be handled under proper radiologically controlled conditions at all times.*

The statistical uncertainty assigned to the certified ratio value is the 95% confidence interval for the unweighted mean of the ratio calculated from assay and mass measurements of the separated isotopes *and* the ratio determined by mass spectrometric measurements of the CRM. The uncertainty is propagated from all known nonnegligible sources of random and systematic variations associated with the measurement methods used.

The plutonium materials used to produce this CRM were obtained from the ORNL Isotope Sales Group with the approval of the DOE Research Materials/Transplutonium Program Committee chaired by J. L. Burnett. Preparation and assay measurements of the CRM and calibration mixtures were performed by C. G. Cacic, NBL; isotopic measurements were performed by D. W. Crawford, NBL; impurity measurements were performed by J. A. Carter and associates, ORNL. Technical assistance was provided by L. A. Machlan, NBS. Isotopic verification measurements were performed by E. L. Callis, ANL. Statistical assessment of the data for certification was performed by M. D. Soriano, NBL. Initial project technical direction was provided by E. L. Garner, NBS; overall direction and coordination of the preparation, certification and issuance of this CRM were provided by N. M. Trahey, NBL.

October 1, 1985
Argonne, Illinois
(Revision of Certificate, dated, 10/1/84)

Carleton D. Bingham
Director

(Over)

The ^{239}Pu and ^{242}Pu separated isotopes ($\geq$99.9% isotopic purity) comprising CRM No. 128 were separately dissolved, chemically purified, and assayed by controlled potential coulometry before being combined by weight. The assay characterization measurements were used to calculate a precise gravimetric $^{239}Pu/^{242}Pu$ value for the CRM. The CRM was then isotopically equilibrated, apportioned, and dried into units. Isotopic certification measurements were performed on CRM units randomly selected according to a statistical sampling plan. The $^{239}Pu/^{242}Pu$ ratio data obtained for the CRM were corrected for mass discrimination effects by concurrent analysis of five $^{239}Pu/^{242}Pu$ calibration mixtures, prepared by weight to closely bracket the isotopic ratio of the CRM. Total element impurity content was determined by spark source mass spectrometry on selected subsamples and is estimated to be 300 $\mu g/g$ plutonium. Although the CRM was americium-free at the time of preparation, the calculated americium ingrowth from the decay of ^{241}Pu present in small amounts in the CRM is 21 $\mu g/g$ plutonium as of October 1, 1984, and will increase at a rate of approximately 5 percent of the total ^{241}Pu per year.

CRM No. 128 had a radioactivity of 2.7×10^6 Bq (73 μCi) per unit as of July 1, 1984, which is dominated by ^{239}Pu and ^{241}Pu.

The change with time in the CRM No. 128 certified ratio is very small, due to the relatively long half-lives of the primary plutonium isotopes. Table I provides decay-adjusted values for the certified ratio at one-year intervals for a five-year period.

TABLE I

CRM No. 128 Yearly Decay-Adjusted $^{239}Pu/^{242}Pu$ Atom Ratio Value

October 1, 1985	October 1, 1986	October 1, 1987	October 1, 1988	October 1, 1989
0.9993_5	0.9993_2	0.9992_9	0.9992_6	0.9992_4

The plutonium isotopic distribution of CRM No. 128 is given in Table II and is for informational purposes only (not certified).

TABLE II

CRM No. 128 Isotopic Distribution (as of October 1, 1984)

Plutonium Isotope:	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{244}Pu
Atom Percent:	0.004	49.947	0.035	0.036	49.978	<0.001

(The half-life values used to calculate the values in Tables I and II are expressed in years: ^{238}Pu — 87.74; ^{239}Pu — 24,119; ^{240}Pu — 6,562; ^{241}Pu — 14.35; ^{242}Pu — 376,300.)

RECOMMENDED PROCEDURE FOR USING CRM NO. 128

Each CRM unit contains 1 $\pm$ 0.03 mg of plutonium and is designated for in-situ dissolution. When converted to solution form, a unit can be used as is. No additional purification of the CRM is required.

Wipe the Teflon bottle with a chamois or damp cloth to dissipate any static charge which may cause expulsion of the material upon opening. Unscrew the cap, add 1N HNO_3 to the CRM concentration desired and carefully warm the bottle to insure total dissolution. *Do not heat the bottle above 150°C because bottle deformation will occur!* Replace and tighten the cap, then allow the bottle to cool before shaking to homogenize contents. Wipe cap and bottle threads each time a portion of the CRM solution is removed from the bottle.

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 947

Plutonium Isotopic Standard

This Standard Reference Material (SRM) is certified as an isotopic standard for use in isotopic measurements of plutonium. SRM 947 consists of approximately 250 mg of plutonium in the form of plutonium sulfate tetrahydrate packaged in a glass microbottle.

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Atom Percent*	0.278 ±0.006	77.089 ±0.022	18.610 ±0.022	2.821 ±0.006	1.202 ±0.004

**As of January 1, 1982, refer to Table 1 for quarterly decay-adjusted values.*

The plutonium isotopic distribution was determined by thermal ionization mass spectrometry at the National Bureau of Standards (NBS) on samples from which americium and uranium were removed. Because high-purity plutonium isotopes have not been used to prepare known synthetic mixtures, the accuracy is dependent on uranium and plutonium exhibiting similar behavior. The observed mass spectrometer data were corrected for mass discrimination effects using data from the analysis of uranium isotopic SRM's that had been analyzed under similar conditions.

SRM 947 contains uranium and americium isotopes, including growing-in daughters of plutonium that are isobaric with the plutonium isotopes. In addition, there may be radiation damage to the glass bottle and the teflon cap liner resulting in small glass slivers. Therefore, in its use, a chemical separation that provides a purified plutonium fraction is essential to the attainment of high accuracy.

Measurements leading to the certification of this SRM were made in the Inorganic Analytical Research Division by E.L. Garner and L.A. Machlan.

The technical and support aspects involved in the revision of this Certificate were coordinated through the Office of Standard Reference Materials by T.E. Gills.

August 19, 1982
Washington, D.C. 20234
(Revision of Certificate
dated 12-3-71)

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

The decay-adjusted values for the plutonium isotopic composition, in atom percent, are tabulated below in Table 1. The half-life values, in years, used for the decay-adjustment are: ^{238}Pu, 87.74; ^{239}Pu, 24,119; ^{240}Pu, 6,560; ^{241}Pu, 14.34; and ^{242}Pu, 387,000.

Table 1
Decay-Adjusted Plutonium Isotopic Composition
Atom Percent

Date	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
January 1, 1982	0.278	77.089	18.610	2.821	1.202
April 1, 1982	.278	77.115	18.616	2.789	1.202
July 1, 1982	.277	77.142	18.622	2.756	1.203
October 1, 1982	.277	77.168	18.628	2.724	1.203
January 1, 1983	.276	77.194	18.634	2.692	1.204
April 1, 1983	.276	77.219	18.640	2.661	1.204
July 1, 1983	.275	77.245	18.645	2.630	1.205
October 1, 1983	.275	77.270	18.651	2.599	1.205
January 1, 1984	.275	77.295	18.657	2.568	1.205
April 1, 1984	.274	77.319	18.662	2.538	1.206
July 1, 1984	.274	77.344	18.668	2.509	1.206
October 1, 1984	.273	77.368	18.673	2.479	1.206
January 1, 1985	.273	77.392	18.679	2.450	1.207
April 1, 1985	.272	77.415	18.684	2.422	1.207
July 1, 1985	.272	77.438	18.689	2.393	1.208
October 1, 1985	.271	77.461	18.694	2.365	1.208
January 1, 1986	.271	77.484	18.700	2.337	1.208
April 1, 1986	.270	77.506	18.704	2.310	1.209
July 1, 1986	.270	77.528	18.709	2.283	1.209
October 1, 1986	.270	77.550	18.714	2.256	1.209
95% Confidence Limit:	±0.006	±0.022	±0.022	±0.006	±0.004

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 949f

Plutonium Metal

(In cooperation with the University of California Los Alamos
National Laboratory, Los Alamos, New Mexico)

This Standard Reference Material is certified for plutonium content and is primarily intended for use in the chemical assay of plutonium. SRM 949f consists of approximately 0.5 gram of plutonium metal that has been sealed in a glass tube under a reduced-pressure argon atmosphere. Each unit is identified by tube number and sample mass.

Plutonium assay in weight percent as of October 1980:[a] 99.99 (99.90-100.00)[b]

Tube No. _____

Mass _____

[a] *See Table 2 for decay-adjusted values.*

[b] *The interval expressing the uncertainty of the certified value includes a one-sided 99% confidence interval for the mean and bounds on the systematic error.*

The plutonium assays were performed by the Los Alamos National Laboratory with collaborative analysis performed at the Department of Energy, New Brunswick Laboratory. The Los Alamos National Laboratory used two titrimetry methods utilizing both photometric and potentiometric end points [1,2,3,4]. The New Brunswick Laboratory used a controlled-potential coulometric method [5,6].

The uncertainty statement for the certified value is a one-sided 99% confidence interval on the mean of the potassium dichromate titrimetric method, which is 99.98-100 percent, expanded by the bound on the systematic error ± 0.08. The uncertainty statement is based upon the potassium dichromate method because adequate systematic error bounds are available. The mean value for the potassium dichromate titrimetric method is 99.999 percent with a standard error on the mean of 0.006 percent based on 16 determinations.

The americium resulting from the decay of 14.35 years plutonium-241 was approximately 71 μg/g as of October 1980. The total of all detected impurities is approximately 115 μg/g.

The technical and support aspects leading to certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. E. Gills.

The statistical assessment of the data for the certification of this SRM was performed by W. Liggett of the Statistical Engineering Division of the National Bureau of Standards.

Washington, D.C. 20234
September 13, 1982
(Revision of Certificate
dated 5-11-82)

George A. Uriano, Chief
Office of Standard Reference Materials

(over)

Supplemental Information

Isotopic Analysis

Plutonium isotopic distribution was determined by thermal ionization mass spectrometry at the Los Alamos National Laboratory. The values given in Table 1 are *not certified,* but are given for information only.

Table 1

Isotope	Isotope Mass	Average Atom % on October 8, 1980
^{238}Pu	238.04942	0.0040
^{239}Pu	239.05208	97.121
^{240}Pu	240.05382	2.804
^{241}Pu	241.05669	0.065
^{242}Pu	242.05864	0.006

Calculated Atomic Wt. 239.082

Notice and Warnings to Users

SRM 949f may contain small pieces of Pu metal that may have become separated from the larger pieces in the tube. It is recommended that the tube be carefully rinsed with 3 M hydrochloric acid during the transfer.

The mass of each sample was determined with an overall accuracy of ± 0.05 mg. The assigned mass for each unit, however, has not been corrected for the buoyancy of the dry argon atmosphere in which the plutonium metal was weighed and packaged. The computed atmosphere buoyancy correction factor for dry argon at 592 mm Hg and 20 °C is 0.99991 for plutonium metal (having a density of 19.7 g/cm^3) relative to brass weights. The value given on this certificate for the mass of the plutonium may be multiplied by this factor to obtain the "true" in vacuo mass.

SRM 949f had a radioactivity of approximately 0.07 Ci per unit, as of October, 1980.

The decay-adjusted values for plutonium in 949f for a 5-year period are shown in Table 2. The half-life values, in years, used for the decay adjustments are ^{238}Pu, 87.74; ^{239}Pu, 24119; ^{240}Pu, 6560; ^{241}Pu, 14.35; and ^{242}Pu, 387,000.

Table 2

Plutonium Assay, Percent

1980	1981	1982	1983	1984
99.99	99.98	99.98	99.97	99.97

References

1. C. E. Caldwell, L. S. Grill, F. J. Miner, and N. E. Moody. Anal. Chem. 34, 346, 1962.

2. G. R. Waterbury and C. S. Metz, Los Alamos Scientific Lab Report, LA 3141, 1965.

3. K. S. Bergstresser, Los Alamos Scientific Lab Report, LA 2859, 1963.

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5. M. K. Holland, J. R. Weiss, and C. E. Pietri, Anal. Chem. 50, 236-240 (1978).

6. D. D. Jackson, R. M. Hollen, F. R. Roensch, and J. E. Rein, Anal. Chim. Acta 117 205-15 (1980.)

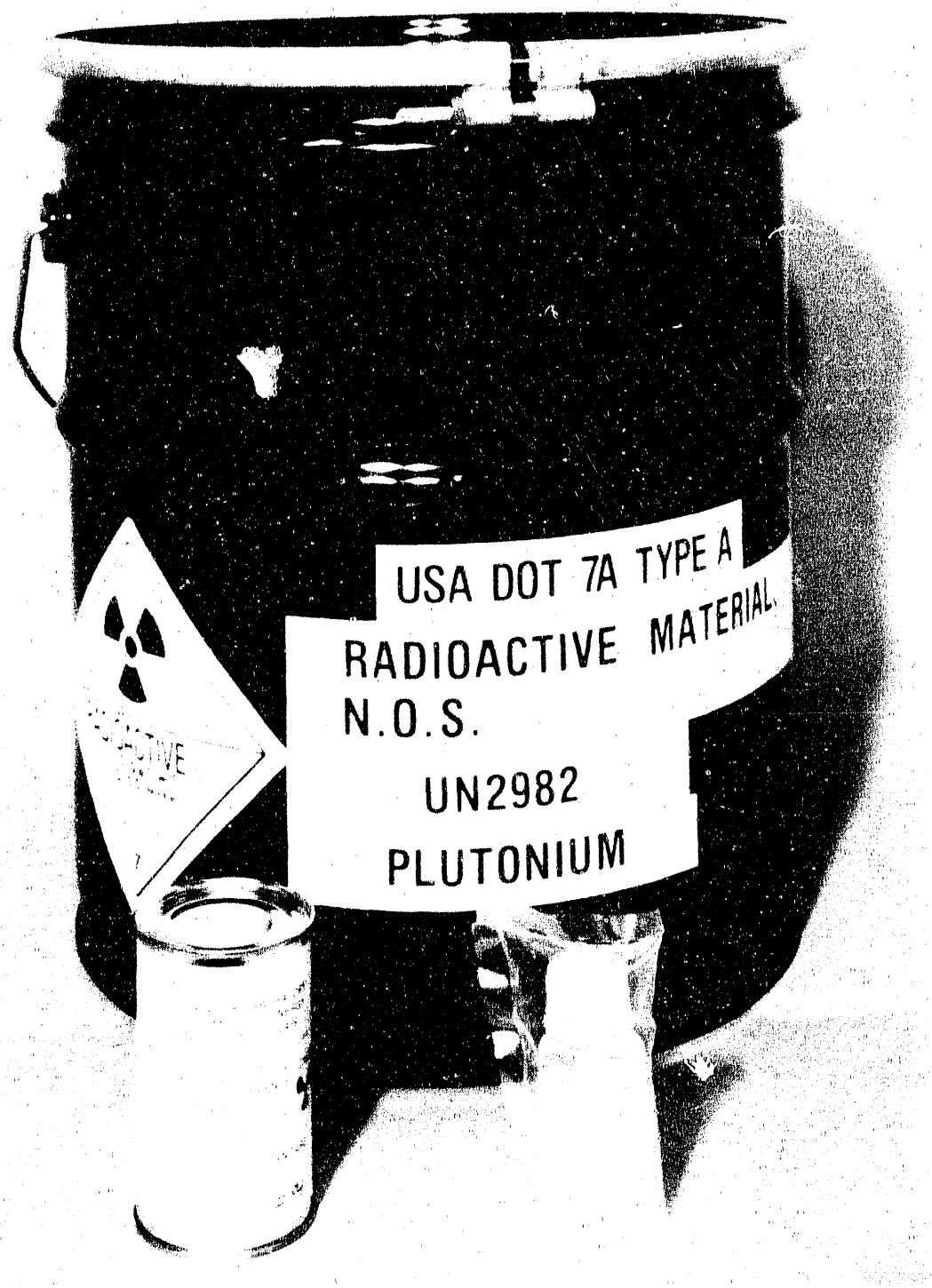

Figure 19. DOE and DOT Approved Shipping Containers for NBL CRM 128

ANNEX I

Isotopic Fractionation Comparisons Between Uranium and Plutonium

The calibration of NBL CRM 128 using NBS SRM 947 (uranium-based) and calibration mixtures (plutonium-based) provided data for experimentally comparing the fractionation corrections between the two elements.

Adaptations of Langmuir's equation, which describes ionic evaporation as functions of ionization potentials of free atoms and work functions of filament surfaces,[19] and Graham's Law relating to diffusion rates and densities of various vapors, form the basis of the static fractionation coefficient, β. Describing the extent of thermal discrimination between two masses or isotopes, β can be defined as follows:

$$\beta = (m_1 - m_2)^{1/2} \qquad (27)$$

where m_1 and m_2 are the atomic masses of two isotopes evaporating from a hot metal surface. In theory, the fractionation correction should resemble the β value obtained from the above equation. However, experimental data from a multiple filament ion source, in which molecular (not atomic) vapors must be considered, indicate that the observed corrections are closer to unity than β. However, β values can be used to compare predicted fractionation bias values between elements.

When the NBS SRM 947 isotopic values were being certified in the 1960's, the fractionation corrections for plutonium were based upon uranium isotopic standards due to the unavailability of synthetic plutonium isotopic mixtures with accurately known isotope ratio values. The calculation of the β values below suggests that the uranium and plutonium isotopes should behave similarly while undergoing thermal ionization.

To eliminate the systematic errors associated with the measurements, and to reduce the random errors from experimental variations between the separate provisional and absolute certification experiments, a double ratio method was used in the comparison. The ratio, β_{Pu}/β_U, was divided by the ratio of the correction factors observed in each experiment. Each correction factor was multiplied by the uncorrected Pu-242/Pu-239 CRM ratio obtained in the counter experiment to dampen and reduce those experimental variations. A value for the double ratio of one would demonstrate identical plutonium and uranium behavior in accordance with theoretical predictions.

$$\text{Plutonium } \beta \text{ Value, } \beta_{Pu} = (\text{m-242/m-239})^{1/2} = 1.00638 \qquad (28)$$

$$\text{Uranium } \beta \text{ Value, } \beta_U = (\text{m-238/m-235})^{1/2} = 1.00627 \qquad (29)$$

This double ratio, γ, is expressed mathematically as:

$$\gamma = (\beta_{Pu}/\beta_U)/(K_{2,9} * R_{2,9}'/K_{2,9}' * R_{2,9}) \qquad (30)$$

where: $K_{2/9}$ = Pu-242/Pu-239 correction factor determined in the absolute certification of NBL CRM 128,

$K_{2/9}'$ = Pu-242/Pu-239 correction factor determined in its provisional certification,

$R_{2/9}$ = uncorrected Pu-242/Pu-239 ratio determined in its absolute certification, and

$R_{2/9}'$ = uncorrected Pu-242/Pu-239 ratio determined in its provisional certification.

Therefore,

$$\gamma = \frac{1.00638}{1.00627} / \frac{1.002155 * 0.008507}{1.002873 * 0.998373} = 1.00069 \qquad (31)$$

The small deviation of γ from unity (~0.07%) supports the static fractionation prediction that uranium and plutonium behave similarly while undergoing thermal ionization.

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1. Gramlich, J. W., Murphy, T. J., Garner, E. L., and Shields, W. R., "Absolute Isotopic Abundance Ratio and the Atomic Weight of Rhenium," J. Res. National Bureau of Standards, 77A, 691-698, (November - December, 1973).

2. Garner, E. L., Murphy, T. J., Gramlich, J. W., Paulsen, P. J., and Barnes, I. L., "Absolute Isotopic Abundance and the Atomic Weight of a Reference Sample of Potassium," J. Res. National Bureau of Standards, 79A, 713-725, (November - December, 1975).

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