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**Uranium Isotopic Composition and
Uranium Concentration in Special
Reference Material SRM A
(Uranium in KCl/LiCl Salt Matrix)**

by D. G. Graczyk, A. M. Essling,
C. S. Sabau, F. P. Smith, D. L. Bowers,
and J. P. Ackerman

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ABSTRACT

To help assure that analysis data of known quality will be produced in support of demonstration programs at the Fuel Conditioning Facility at Argonne National Laboratory-West (Idaho Falls, ID), a special reference material has been prepared and characterized. Designated SRM A, the material consists of individual units of LiCl/KCl eutectic salt containing a nominal concentration of 2.5 wt. % enriched uranium. Analyses were performed at Argonne National Laboratory-East (Argonne, IL) to determine the uniformity of the material and to establish reference values for the uranium concentration and uranium isotopic composition. Ten units from a batch of approximately 190 units were analyzed by the mass spectrometric isotope dilution technique to determine their uranium concentration. These measurements provided a mean value of 2.5058 ± 0.0052 wt. % U, where the uncertainty includes estimated limits to both random and systematic errors that might have affected the measurements. Evidence was found of a small, apparently random, non-uniformity in uranium content of the individual SRM A units, which exhibits a standard deviation of 0.078% of the mean uranium concentration. Isotopic analysis of the uranium from three units, by means of thermal ionization mass spectrometry with a special, internal-standard procedure, indicated that the uranium isotopy is uniform among the pellets with a composition corresponding to 0.1115 ± 0.0006 wt. % ^{234}U , 19.8336 ± 0.0059 wt. % ^{235}U , 0.1337 ± 0.0006 wt. % ^{236}U , and 79.9171 ± 0.0057 wt. % ^{238}U .

I. INTRODUCTION

Reference materials having uniform composition and well-characterized properties play an important role in any quality assurance program aimed at maintaining statistical control of a measurement process.¹ Appropriate reference materials provide the basis for evaluating and validating analysis methods or procedures; permit the long-term monitoring of method performance through control charts or other statistical tools based on periodic analysis of samples having predictable values for the parameters to be measured; and help establish comparability of data generated by different methods or different laboratories for a specific parameter.²

Recognizing the value of appropriate reference materials to assuring analysis data of known quality, the Analytical Laboratory at Argonne National Laboratory-West (ANL-W) arranged for preparation of specific reference materials, which would simulate samples anticipated from operations related to the electrometallurgical conditioning of spent nuclear fuel at the ANL-W site. One of these Special Reference Materials (SRMs), designated SRM A, was constituted to contain a nominal concentration of 2.5 weight percent (wt. %) enriched uranium in a matrix of potassium chloride/lithium chloride (KCl/LiCl) eutectic salt. The SRM A material was prepared by the Chemical Technology Division (CMT) at Argonne National Laboratory-East (ANL-E) and has been analyzed by the ANL-E Analytical Chemistry Laboratory (ACL) to determine the uniformity of composition of the material and to establish reference values for the uranium concentration and uranium isotopic composition. This report describes the approach taken by the ACL in selecting samples for analysis, describes ACL methodology for preparing and analyzing the samples for uranium, and presents the results of the characterization measurements along with estimates of the uncertainty associated with the measured values.

II. DESCRIPTION OF SRM A

The Special Reference Material SRM A was prepared in the CMT at ANL-E according to specifications established in collaboration with the Analytical Laboratory at ANL-W. For this preparation, appropriate quantities of KCl/LiCl eutectic salt and uranium metal (approximately 19.8 wt. % ^{235}U) were placed in an apparatus (see Figure 1) designed to allow heating of the salt to its molten state, mixing of the molten salt, adding CdCl_2 oxidant to bring the uranium metal into solution in the salt as UCl_3 , and dispensing the salt mixture into individual small portions (nominally one gram). All operations involved in preparing and dispensing the molten salt mixture were performed in an argon-atmosphere glovebox to protect the product from moisture or other deleterious atmospheric contaminants. The molten salt mixture was heated with intermittent mixing over a period of 14 days to ensure complete equilibration of uranium in the system and uniform salt composition. During this time, several salt portions were dispensed from the apparatus; some of these were analyzed for uranium to monitor the completeness of mixing and equilibration. When confidence in the batch uniformity was achieved, the group of samples comprising SRM A was dispensed over a four-day period. Table 1 summarizes the composition and history of the molten salt batch prepared for SRM A.

The material designated as SRM A consists of a group of 190 individual samples of KCl/LiCl eutectic salt containing uranium chloride in an amount that corresponds to a nominal concentration of 2.5 wt. % uranium as the element. Each of the approximately one-gram portions of salt was dispensed into a numbered tantalum cup, with cup numbers ranging from A-10 through A-199. Samples with numbers below A-10 were dispensed during the period of mixing and equilibration of the salt batch and were not considered to be representative of the final SRM A material.

After the individual SRM A salt portions had been dispensed into their tantalum cups, they were packaged in groups of five in spring-loaded stainless-steel tubes that were sealed with Swagelok closures. These storage tubes were labeled to identify the cups contained in each and were stored in the argon-atmosphere glovebox until characterization of the SRM was complete.

One group of five samples (A-44 through A-48) was used for preliminary analysis to assess the quality of the batch and to test analysis procedures for the SRM characterization measurements. Several modifications to the analysis procedures were implemented as a result of experience gained with these samples. Because of potential deficiencies in our handling of these samples, results obtained with them are not reported. Ten other SRM A samples were used in the final characterization measurements on the SRM A batch. The sealed tubes containing the remainder (175 samples) of the batch were ultimately removed from the argon-atmosphere glovebox, cleaned to remove external contamination, and transferred to the Analytical Laboratory at ANL-W.

Figure 1. Schematic Diagram of Apparatus for Preparing and Dispensing Portions of Salt Mixture.

Table 1. Composition and History of Molten Salt Batch Prepared for SRM A.

Event	Date	Approx. Time (Start)	Days Heated	Cumulative Hours Stirred
Add 916.59 g LiCl/KCl Salt	10/05/92	--	--	--
Drop ~3 g Salt	10/09/92	--	--	--
Add 24.011 g U and 27.3 g CdCl ₂	11/16/92	--	--	--
Begin Heating	11/17/92	9:13	0	0
Stir 2 h	11/17/92	14:00	0	2:00
Stir 6 h 50 min	11/18/92	9:02	1	8:50
Stir 6 h 05 min	11/19/92	8:45	2	14:55
Stir 10 min	11/20/92	8:50	3	15:05
Stir 1 h	11/20/92	10:50	3	16:05
Dispense Samples A-1 and A-2	11/20/92	13:45	3	16:05
Dispense Samples A-3 and A-4	11/20/92	14:15	3	16:05
Stir 1 h 06 min	11/23/92	8:39	6	17:11
Dispense Samples A-5 and A-6	11/23/92	11:05	6	17:11
Stir 2 h 45 min	11/23/92	13:15	6	19:56
Stir 1 h 55 min	11/24/92	8:45	7	21:51
Dispense Sample A-7	11/24/92	11:00	7	21:51
Stir 2 h 45 min	11/24/92	13:05	7	24:36
Stir 39 min	11/25/92	8:38	8	25:15
Dispense Sample A-8	11/25/92	9:45	8	25:15
Stir 2 h 20 min	11/30/92	13:25	13	27:35
Stir 2 h 33 min	12/01/92	8:57	14	30:08
Dispense Samples A-10 through A-46	12/01/92	13:10	14	30:08
Stir 20 min	12/02/92	9:00	15	30:28
Dispense Samples A-47 through A-81	12/02/92	10:00	15	30:28
Dispense Samples A-82 through A-118	12/02/92	15:00	15	30:28
Dispense Samples A-119 through A-153	12/03/92	11:00	16	30:28
Dispense Samples A-154 through A-189	12/04/92	10:00	17	30:28
Dispense Samples A-190 through A-199	12/04/92	15:00	17	30:28

III. SAMPLING AND ANALYSIS PLAN FOR SRM A CHARACTERIZATION

The goal of the SRM A characterization measurements performed by the ACL at ANL-E was to provide analytical data that would permit an evaluation of whether the batch of samples was uniform in composition and would establish reference values for the uranium concentration and uranium isotopic composition in the batch. To test for batch uniformity, we elected to measure the uranium concentration in ten of the SRM A units. Because nonuniformity in the batch might show itself as a gradual uranium-concentration change in the SRM stock material over the time it took to dispense all the units, we opted to choose samples at essentially constant intervals over the pour sequence rather than selecting units at random. Hence, units designated for uranium assay measurements included the first and last in the pour sequence (units A-10 and A-199) and eight other units equally spaced between these (units A-31, A-52, A-73, A-94, A-115, A-136, A-157, and A-178). To avoid unnecessary handling of the SRM units, these designated units were not specifically sought after when individual units were retrieved for analysis from their storage tubes. Rather, we selected the top unit in each storage tube that contained one of the designated samples; in this way, we avoided having to remove and replace other units in the tube. With this selection process, the units taken for analysis were A-14, A-34, A-53, A-73, A-97, A-117, A-137, A-157, A-179, and A-199.

The uranium isotopic composition in the SRM A material was determined by thermal-ionization mass spectrometry (TIMS) after isolation and purification of a portion of the uranium in a given unit. Mass spectrometric determination of the ratio of major isotopes (^{235}U and ^{238}U) was performed with the ACL "internal-standard" procedure.^{3,4} In this procedure, isotopic fractionation during the TIMS analysis is corrected for by measurement of the ratio of ^{234}U to ^{236}U in a precisely characterized spike, which is placed with the unknown sample on the TIMS filament when it is prepared for loading into the mass spectrometer for analysis. This procedure provides uranium isotope ratio values with a typical precision of <0.01% relative standard deviation (RSD) and direct traceability to the National Bureau of Standards Standard Reference Material (NBS SRM) U-500, which was used in establishing the $^{234}\text{U}/^{236}\text{U}$ reference ratio in the internal standard spike.* Ratios involving minor isotopes (^{234}U , ^{236}U) in the SRM A uranium were corrected for isotope fractionation during analysis by normalizing the ratios to the ratio of major isotopes obtained with the added internal standard. Because the isotopic composition of the uranium in the SRM A units is not likely to differ from one unit to another and because the measurements proposed for the isotopic analyses were expected to show high precision, only three SRM units were selected for isotopic analysis. These units were A-97, A-179, and A-199. Multiple measurements (at least duplicate) on each uranium sample were made to allow assessment of the measurement precision.

* The National Bureau of Standards has changed its name to the national Institute of Standards and Technology (NIST), and the uranium isotopic SRM U-500 is now distributed by the New Brunswick Laboratory (NBL) under the designation of NBL Certified Reference Material (CRM) U500. The certified reference values for the isotopic composition of NBS SRMs now being distributed by NBL have not been changed from the NBS values. Because the reference material in our laboratory was procured from NBS while it still existed, we refer to it in this report as NBS SRM U-500. It is to be understood that this material is identical to NBL CRM U500 with regard to establishing traceability of isotope-ratio measurements.

The concentration of uranium in each of ten SRM A units was determined by mass spectrometric isotope dilution (MSID) assay using NBL CRM-111A (^{233}U) as the spike and the internal-standard procedure for making fractionation corrections during the mass spectrometric measurements to determine isotope ratios. The salt plug from each unit was weighed and dissolved, and each solution was analyzed in duplicate to allow assessment of the analysis precision. Unit-to-unit variance in excess of the analysis variance was attributed to SRM nonuniformity, after taking into account variance estimated for weighing of the salt samples.

Uncertainties in the reference values assigned to SRM A from the ACL measurements were estimated from statistical analysis of replicate data obtained during the characterization measurements and from consideration of potential systematic errors that might apply from uncertainties in reference materials, equipment calibrations, or other sources.

IV. OPERATIONS

A. Preparation of Isotope Dilution Spikes

Spikes for the isotope-dilution uranium assays of SRM A were prepared from the ^{233}U Uranium Spike and Isotopic Solution Standard, CRM-111A, which we obtained from the New Brunswick Laboratory (Argonne, IL). Each CRM-111A unit consists of approximately 5 mg of uranium (99.4911 ± 0.0006 at. % ^{233}U) dissolved in 10 g of 0.8 N HNO_3 . This solution is contained in a sealed glass ampule. Both the uranium concentration and the isotopic composition of uranium in the solution are certified.

In preparing the spikes used in the SRM A uranium assays, we diluted the solution from a CRM-111A ampule, by weight, to obtain a stock solution containing a known concentration of approximately 20 $\mu\text{g U}$ per gram of solution, and then distributed this solution, as weighed portions containing about 50 $\mu\text{g U}$ each, into precleaned 30-mL Pyrex beakers. All weighings were made to the nearest 0.0001 g. The dispensing of aliquots of the stock solution was accomplished with a platinum-tipped Pyrex weight buret and a Mettler AK-160 balance interfaced to our PDP-11 computer system. The dispensing operations were carried out with the aid of an interactive computer program that directs analyst operations with the weight buret, reads the balance and records individual weighings, and calculates the quantity of uranium in each spike from the weight of solution dispensed and the concentration of uranium in the stock solution as determined from the certified value for the CRM and dilutions made when the stock solution was prepared. The solution in each spike beaker was ultimately evaporated to dryness at low heat (90 to 95°C), and each beaker was covered with Parafilm. The spike beakers were then placed in polyethylene storage boxes in a locked safe until needed for the SRM A assay operations.

To verify reliability of the spike preparations, we determined the quantity of CRM-111A uranium in three of the spike beakers by MSID using NBS SRM 950a as the isotope-dilution spike. For these assays, weighed portions of a stock solution containing a known concentration of NBS SRM 950a uranium were added to each of the three CRM-111A beakers. The NBS SRM 950a is a natural uranium assay standard (oxide form) having a certified uranium concentration with an uncertainty that does not exceed 0.02%, relative, at a confidence level of at least 95%. After the NBS SRM 950a solution was added to the CRM-111A spike, the solution was evaporated to dryness in the spike beaker, the residue was dissolved in 0.5 mL of concentrated, Instra-Analyzed nitric acid (J. T. Baker Chemical Co.), and the material was taken to dryness again. The resulting mixture of isotopes was analyzed by mass spectrometry with the internal standard procedure (see Sec. IV.C), and the CRM-111A content of the beaker was calculated from the amount of NBS 950a uranium added to the beaker. Results of these assays are given in Table 2, which shows the quantity of CRM-111A uranium recorded as having been added to each beaker during preparation of the spikes, the quantity of CRM-111A found in each beaker from the assay versus NBS SRM 950a, and the percent recovery of the CRM-111A uranium.

Table 2. Results of Verification Measurements on CRM-111A Spikes
(MSID Assay Versus NBS SRM 950a).

Spike No.	Added CRM-111A Uranium, μg	Found CRM-111A Uranium, μg	Recovery, %
W233-012	49.8356	49.8014	99.93 ₁
W233-013	51.0085	50.9924	99.96 ₈
W233-014	51.8399	51.7970	99.91 ₇
Average:			99.93 ₉
RSD:			$\pm 0.026\%$

Given the uncertainties in the reference materials involved in these measurements ($\pm 0.02\%$, relative, for SRM 950a; $\pm 0.025\%$, relative, for CRM-111A) and the level of imprecision of the three measurements made (0.026% RSD), the difference between the added and found values for the CRM-111A uranium in these spikes, 0.061%, relative, was judged to be small enough to verify that errors in the handling or preparation of the spike were absent. For MSID assays with these CRM-111A spikes, we used the uranium spike quantities determined from the certified reference concentration of the CRM in our calculations. To account for the difference between this uranium quantity and the quantities we determined with MSID using NBS 950a, we include a term in our estimated uncertainty for the SRM A uranium assays that corresponds to the 0.061% difference observed between the quantity recorded for each beaker and the quantity found. This term was assigned a value $0.061 \pm 0.065\%$, which we estimated as $\bar{x} \pm t \cdot s / \sqrt{N}$ where $\bar{x}$ is the average difference (0.061%), t is the Student's t parameter for two degrees of freedom and 95% confidence limits, and $N (=3)$ is the number of measurements from which the average was determined.

We also analyzed the uranium in one spike beaker to determine its isotopic composition and thereby verify that we did not change the spike isotopy by contamination during our handling of the CRM. Results of our isotopic analysis of this spike are summarized in Table 3. Our measured ratios for the minor isotopes in the CRM-111A spike uranium show excellent precision but exhibit a negative bias relative to the NBL certified values. The sign of this bias is inconsistent with our having contaminated the spike uranium during handling, since it would require contamination with ^{233}U -enriched uranium of higher isotopic purity than the CRM-111A uranium. The magnitudes of the differences between our measured ratios and the NBL values range from 8 to 16 parts per million (ppm) in the individual ratios and might be indicative of different baseline or linearity corrections applied in our measurements as compared to the NBL measurements. From a practical standpoint,

Table 3. Measurement Results from Isotopic Analysis of Uranium in CRM-111A Spike.

Run No.	Measured Atom Ratio of Uranium Isotopes			
	238/233	236/233	235/233	234/233
1	0.002290	0.000152	0.000780	0.001848
2	0.002286	0.000150	0.000780	0.001848
Average	0.002288	0.000151	0.000780	0.001848
NBL Atom Ratios ^a	0.002298	0.000167	0.000794	0.001856
ANL-NBL ^b	-0.000010	-0.000016	-0.000014	-0.000008

^aValues calculated from atom percent abundances given on the CRM-111A Certificate of Analysis.

^bAverage of measured values minus value calculated from NBL values from CRM-111A Certificate of Analysis.

differences of this magnitude in the minor isotope concentrations for the MSID spike have a negligible effect on the SRM A uranium assays performed with this spike material. On this basis, we judged these data to satisfactorily demonstrate the absence of spike contamination. For our MSID assay calculations, we used the isotopic composition given by NBL on the CRM-111A certificate to describe parameters related to the spike isotopy. Had we used our own data for the minor isotopes, the assay results would be virtually unchanged (each assay result would increase by about 0.01% of the reported value).

B. Preparation of SRM A Samples for Analysis

In preparing individual SRM A units for analysis, the units were first transferred from the glovebox in which they were prepared to a nearby laboratory. Then, the salt pellet in each unit was weighed and dissolved, and portions of this solution were aliquoted, by weight, to provide samples for mass spectrometric analysis. Some of the sample aliquots were weighed into CRM-111A spikes for MSID uranium assay; others were designated for isotopic analysis and were simply weighed into clean, empty beakers. In all cases, uranium in the aliquot was separated from the KCl/LiCl salt matrix by column-extraction chromatography to isolate and purify the uranium fraction for analysis by mass spectrometry. Details of these operations are described in this section.

1. Transfer and Weighing of Salt Pellets

The SRM A units were transferred from their argon-atmosphere glovebox when requested by the analytical chemistry operations personnel to ensure rapid handling and minimal exposure of the specimens to atmospheric moisture or other contaminants. To facilitate and expedite handling of the specimens in the laboratory, each specimen selected for analysis was moved, in the glovebox, from its closed storage tube to a wide-mouth, 1-oz. (30-mL) polyethylene bottle (Nalgene). This bottle type was selected for the transfer because the rim of the tantalum cup that held each SRM A salt pellet could sit on the mouth of the bottle and prevent the cup from going inside. When the tantalum cup was placed at the top of the bottle and the cover was screwed on, movement of the salt pellet was limited, which protected the pellet from breaking apart during transfer. In addition, the position of the specimen at the opening to the bottle made it easier to transfer the salt pellet to a dissolution vessel in the first step of the laboratory operations.

The ten SRM A units that were selected for analysis were transferred from the glovebox to the laboratory in two groups of five units. The first group included units numbered A-97, A-117, A-137, A-157, and A-179. This group also included two test-pour specimens that were used in a test to evaluate the influence of moisture pickup by the hygroscopic salt on our weighing of the individual specimens. The second group of specimens contained units numbered A-14, A-34, A-53, A-73, and A-199. When a group of specimens was requested by the laboratory analysts, the bottles containing the specimens were sealed in a polyvinylchloride (PVC) pouch and removed from the glovebox.

When the specimens arrived at the analysis laboratory, each was weighed into a polyethylene bottle for subsequent dissolution. To determine its mass, a selected salt pellet was first taken with forceps from its transfer container [1-oz. (30-mL) wide-mouth bottle] and placed into a narrow-mouth, 4-oz. (120-mL) Nalgene bottle that had been preweighed. This transfer was easily made because the salt pellets did not adhere to the tantalum cups. The 4-oz. (120-mL) bottle containing the salt pellet was immediately reweighed and set aside while any remaining specimens in the group were transferred and weighed. The mass of each pellet was subsequently calculated as the difference between the mass of the bottle and pellet and the bottle tare. Because of the hygroscopic nature of the salt, all specimens in a group were transferred and weighed as quickly as possible to minimize weighing errors associated with moisture pickup during handling of the specimens.

Measurements were made with the two test-pour specimens to evaluate the extent to which moisture pickup during these weighing operations might have affected the values obtained for the specimen weights. For these measurements, a test-pour salt pellet was transferred to a preweighed 4-oz. (120-mL) narrow-mouth bottle like that used for the SRM A specimens, and the weight of the bottle plus pellet was measured at various times following the initial weighing. Results of the moisture-pickup monitoring tests are summarized in Table 4, which presents data that were recorded over the first 34 or 35 min of each pellet's exposure to the atmosphere. Water pickup by the pellets is apparent over this time period, but notably, no significant change in pellet mass was seen in the first 3-5 min of exposure for either specimen. Because the transfer and weighing operations for the SRM A specimens required less than 30 sec to perform, we may be confident that moisture pickup by these specimens prior to determining their mass was negligible.

Table 4. Moisture Pickup by Test Specimens Exposed to Ambient Air.

Trial	Time after Initial Weighing, min	Specimen Mass, ^a g	Weight Gain, ^b g
First Specimen	0	0.9105	0.0000
	3	0.9106	0.0001
	12	0.9118 ₅	0.0013 ₅
	22	0.9135 ₅	0.0030 ₅
	34	0.9142	0.0037
Second Specimen	0	0.5908 ₅	0.0000
	5	0.5907	-0.0001 ₅
	13	0.5911 ₅	0.0003
	23	0.5919	0.0010 ₅
	35	0.5927	0.0018 ₅

^aMass of bottle plus pellet minus bottle tare; each value obtained as average of two balance readings.

^bSpecimen mass at corresponding time minus specimen mass from initial weighing.

All weighings associated with preparing the SRM A salt samples for analysis were performed with a Mettler Model AE-200 balance, having a readability of 0.1 mg, and a hard-copy tape printer for recording the balance readings. Typically, two or more readings were obtained for each weighing operation, and they were averaged to give the value used for the mass of the object being weighed. Performance of this balance was tested each day that measurements related to the SRM A samples were made. For these tests, balance readings were obtained with secondary standard weights (nominal mass of 1, 5, and 10 g), which were calibrated by comparison with standard weights that had been individually calibrated by the U.S. National Bureau of Standards (NBS 224178/B; calibrated February 1981).

Results from these balance performance tests are summarized in Table 5, which shows average readings and standard deviations for the readings obtained on a given day and on different days for each test weight. From the average of all readings with each test weight, we found a small positive bias (+0.24 mg) in the measured mass of the 5-g test weight and much smaller apparent biases (+0.07 mg in each case) for the 1-g and 10-g weights. The larger bias for the 5-g weight might indicate a trace of dirt or corrosion on this working standard, which occurred after its reference mass was determined. Considering that this larger bias could also reflect a real bias in determining a mass with the balance used, we include in our uncertainty estimate for SRM A uranium assays a term that allows for a potential bias of +0.3 mg in each mass measurement.

Table 5. Summary of Results from Balance Performance Tests during Weighings Related to SRM A Sample Processing.

Test Weight, ^a g	Reference Mass, ^b g	Average Reading, ^c g	Bias, ^d g	Daily Std. Dev. ^e	Day-to-Day Std. Dev. ^f	Total Std. Dev. ^g
1	1.0002 ₆	1.0003 ₃	+0.0000 ₇	0.0001 ₀	0.0001 ₄	0.0001 ₇
5	5.0001 ₅	5.0003 ₉	+0.0002 ₄	0.0001 ₀	0.0000 ₆	0.0001 ₂
10	10.0002 ₅	10.0003 ₂	+0.0000 ₇	0.0001 ₄	0.0001 ₂	0.0001 ₈
			RMS Std. Dev. ^h	0.0001 ₁	0.0001 ₁	0.0001 ₆

^aNominal mass of test weight.

^bDetermined by comparison weighing versus NBS calibrated weights.

^cAverage value of all readings obtained with test weight during processing of SRM A samples.

^dDifference between average reading and reference mass.

^ePooled standard deviation of readings for test mass on a given day.

^fStandard deviation of average readings obtained on different days.

^gRoot-mean-square sum of daily and day-to-day standard deviations.

^hRoot-mean-square value for standard deviations in corresponding column.

The repeatability and reproducibility of weighings with the test weights were independent of the test mass, as demonstrated by the daily and day-to-day standard deviations in Table 5. From these data, we estimate the standard deviation of a single mass measurement with this balance to be ± 0.00016 g, which includes both the daily and day-to-day variance contributions. Overall, the balance performance was quite satisfactory, with accuracy and precision at levels conforming to typical operations with comparable instruments in good working order.

2. Dissolution of Salt Pellets and Preparation of Samples for Mass Spectrometry

After a group of salt pellets had been weighed, approximately 100 mL of 2 N nitric acid was added to each of the polyethylene bottles that contained the weighed specimens. Then, each bottle was allowed to stand, with occasional mixing of its contents, until the following day. This step allowed the salt specimen to dissolve completely and the solution to equilibrate with ambient conditions.

After standing overnight, each bottle was weighed and then shaken to mix the specimen solution. Next, duplicate 3-g aliquots of each stock solution were weighed into tared, 2-oz. (60-mL) Nalgene bottles and diluted with 2 N nitric acid to 50 g for use in preparing samples for MSID uranium assay. If the specimen at hand was designated for uranium isotopic analysis, 2-3 g of the primary stock solution (0.5-0.75 mg U) was also aliquoted into a new, precleaned, 30-mL beaker for subsequent isolation and purification of its uranium and mass spectrometric isotopic measurements on the uranium fraction.

One 3-g aliquot from each of the duplicate dilutions of the stock solution was weighed into a beaker containing one of the previously prepared CRM-111A spikes described in Sec. IV.A. The dilutions performed and aliquots taken were selected to provide convenient handling (i.e., reasonable solution volumes), sufficient mass to minimize the effects of weighing uncertainties, and a match between the quantity of uranium in the ^{233}U spikes and the quantity of sample uranium added to each spike. The approach to weighing individual specimens, dissolving them, and dispensing aliquots of the solutions was carefully planned to avoid any need for quantitative transfers from one container to another, and thereby eliminating error contributions associated with such transfers.

After the appropriate solution aliquots were weighed, they were treated to ensure complete isotopic equilibration between sample and spike uranium and to isolate and purify the uranium for mass spectrometric analysis. The same treatment was applied to both isotopic and assay (spiked) samples. First, the beakers were placed on a hot plate at low heat, and the aliquoted solutions were taken to dryness. Then, a few milliliters of 8 N nitric acid was added to each beaker, and this solution was also gently evaporated to dryness. For uranium, this treatment is sufficient to achieve isotopic equilibration by converting all of the uranium to uranyl ion.

The beakers were then removed from the hot plate and allowed to cool. Residue in each beaker was dissolved in 1 mL of 2 N nitric acid and transferred to a U/TEVA•Spec column (EIChroM Industries, Darien, IL, Part No. UT-C50, Lot No. 022592), which had been previously conditioned with about 15 mL of 2 N HNO_3 . The beaker was then rinsed twice with 1-mL portions of 2 N nitric acid. Each rinse was also added to the U/TEVA•Spec column, with the column allowed to drain between additions. The column was then washed with six 2-mL additions of 2 N nitric acid. The effluent from these washings contained matrix elements from the salt specimens and was discarded. Uranium retained by the column packing was eluted by adding three 3-mL volumes of 0.01 N HNO_3 , which were collected in a clean, new 10-mL beaker. The solution in the 10-mL beaker was evaporated to dryness. Then, a few milliliters of 0.5 N HNO_3 was added to the beaker, and the solution was evaporated to dryness again to ensure chemical equilibration of the uranium isotopes in the sample. Finally, the beaker was covered with Parafilm and transferred to the mass spectrometry laboratory for isotopic analysis.

C. Mass Spectrometric Measurement of Uranium Isotope Ratios

Uranium isotope ratios needed for determining the isotopic composition of uranium in SRM A, and for assaying the uranium by the isotope-dilution technique, were measured by TIMS with a V.G. Isomass, Model 54R, mass spectrometer system. This instrument is fully automated and capable of sequentially analyzing up to 16 samples without operator intervention once the measurement sequence is initiated. It features fixed source and collector slits; a 16-position, rotating-turret source pumped with a 270 L/s turbomolecular pump; a single-detector configuration with deep-Faraday-cup and Daly-scintillation collector options; and a digital integrator readout circuit. Operation of the instrument is controlled by a Hewlett-Packard (HP) 9845B desktop computer having 187 kilobytes of memory, two integral tape drives, and a floppy disk.

In TIMS, ions are produced at the surface of an electrically heated filament in the mass spectrometer ion source. In applying the TIMS method, one may deposit a small amount of a sample containing the element of interest directly on the ionizing filament (the so-called single-filament configuration), where the sample is evaporated and ionized simultaneously. Alternatively, the sample may be loaded on and evaporated from a second filament, which is heated independently of the ionizing filament (the multiple-filament configuration). In either case, the observed ratio of ion currents corresponding to a ratio of isotopes in the sample may differ from the true ratio of isotopes, largely as a result of isotopic fractionation associated with preferential evaporation of lighter isotopic species. The conventional TIMS technique uses reference materials with known isotopic composition to empirically determine corrections for the bias errors associated with this fractionation. For this approach to be successful, a number of experimental variables must be held constant from run to run, so that corrections determined from the standards will apply equally well to unknown samples analyzed under corresponding conditions. Among these variables are (1) the chemical form of the loaded sample, (2) the quantity of sample deposited on the filament, (3) the type of filament materials, and (4) instrument operating conditions during the course of each analysis.

Because maintaining all of these variables under tight control can be difficult, especially with unknown samples whose purity and quantity can be uncertain, our laboratory has adopted, for uranium, a non-conventional procedure for making fractionation corrections. This procedure uses a reference ratio measured during the analysis as the basis for corrections applied to other ratios measured in the same analysis. The theory and application of this approach have been described elsewhere.⁴ In the case where a desired ratio involves abundant (i.e., major) isotopes in a sample containing ^{233}U , ^{235}U , and/or ^{238}U , we add to the sample on the filament an internal-standard spike of accurately known isotopic composition, which includes ^{234}U and ^{236}U in a nearly 1:1 ratio. During each scan of the isotopes in a mass spectrometer run, the observed ^{234}U -to- ^{236}U ratio is used to determine the magnitude of the fractionation corrections to apply, and appropriate corrections are applied to other isotope ratios measured in the same scan. This "internal-standard" approach to correcting for fractionation effects provides exceptional precision for the uranium isotopic measurements, because the fractionation correction that is determined applies to conditions that exist at each point during the analysis regardless of the operating conditions.

To apply the internal-standard approach to correcting for fractionation, it is necessary that the isotopic composition of the unknown sample be fairly well-known, so that contributions to the internal-standard reference peaks from minor isotopes in the sample can be accounted for. To obtain this sample isotopic information, we analyzed each SRM A isotopic sample by the conventional (i.e., external standard) procedure. After the ratio of major isotopes (i.e., the $^{235}\text{U}/^{238}\text{U}$ ratio) in the SRM A was determined with the internal-standard procedure, we reprocessed the data from these conventional runs to normalize all the measured ratios to the average $^{235}\text{U}/^{238}\text{U}$ value from the internal-standard runs.

The reference value for the $^{234}\text{U}/^{236}\text{U}$ internal-standard mixture was determined in our laboratory by applying the internal-standard approach with NBS U-500 as the internal-standard spike.⁵ Hence, all of the isotope ratios determined with the $^{234}\text{U}/^{236}\text{U}$ spike material are traceable to the certified $^{235}\text{U}/^{238}\text{U}$ ratio in this NBS Standard Reference Material.

Operations in the mass spectrometry laboratory followed the ACL Standard Operating Procedure for isotopic analysis of uranium. Uranium samples were received in the TIMS laboratory in the form of dried nitrate salt in 10-mL Pyrex beakers, each of which contained 0.5 to 0.75 mg U for isotopic samples or approximately 100 μg U for isotope-dilution assay samples. Uranium isotopic standards are kept in the laboratory as solutions, 1.0 mg U per mL in 0.8 N HNO_3 , stored in Teflon bottles.

Our procedure for loading samples for TIMS analysis is applied identically for samples or standards. For samples, however, the procedure starts by first dissolving the nitrate salt in 0.8 N HNO_3 to provide a concentration similar to the standard solutions. To prepare the TIMS sample, an aliquot of the uranium solution containing $1.0 \pm 0.2 \mu\text{g}$ U is deposited on a tantalum mass-spectrometer filament, by using a micro-syringe fitted with a disposable Teflon tip. For samples designated for internal-standard analysis, a 0.5- μL aliquot ($\sim 0.5 \mu\text{g}$ U) of the ANL $^{234}\text{U}/^{236}\text{U}$ internal-standard spike solution is added to the sample drop on the filament, which is sized to contain 0.5 μg of the sample uranium. The solution on the filament is then evaporated to dryness, and the uranium is oxidized by passing a current through the filament. A programmable sample drier controls this heating step. The drying procedure involves heating the filament at 0.5 A for 10 min, followed by 1-min intervals at 1.0, 1.5, and 1.8 A.

The loaded sample filament is next incorporated, together with a second, blank, tantalum side filament and a rhenium ionizing filament, into a triple-filament ionization assembly for subsequent insertion into the TIMS source.

Isotope ratio measurements are performed under computer control. For the SRM A uranium samples, analysis conditions included an ionizing-filament temperature corresponding to a ^{187}Re ion current of 1×10^{-12} A and uranium ion currents measured by peak-jumping with the deep Faraday-cup detector. Conventional isotope ratio measurements were made with a total uranium ion current of 3×10^{-11} A; internal-standard runs were made with measurements at a total uranium ion current of 5×10^{-11} A.

V. RESULTS

A. Uranium Isotopic Composition in SRM A

The isotopic composition of uranium in SRM A was calculated from isotope ratios determined by thermal-ionization mass spectrometry. To ensure high precision and accuracy in the TIMS measurements of individual ratios, we applied an analysis scheme that first employed the internal-standard procedure (see Sec. IV.C) for determining the ratio of major isotopes in the SRM uranium ($^{235}\text{U}/^{238}\text{U}$), and then normalized the ratios for the minor isotopes ($^{234}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$) to the average value for $^{235}\text{U}/^{238}\text{U}$ that was obtained from the internal-standard runs. Because the isotope mixture in the internal-standard spike is calibrated against the certificate value for $^{235}\text{U}/^{238}\text{U}$ in the Standard Reference Material U-500, this scheme provides corrections for isotope fractionation in the TIMS measurements that are directly traceable to the U-500 certificate value for $^{235}\text{U}/^{238}\text{U}$. To verify reliable performance of the internal-standard and internal-normalization procedures, and to provide data for assessing potential residual bias in the measured ratios, we analyzed several samples of SRM U-500 in the same time period as the SRM A isotopic samples were analyzed. To evaluate performance of the methods for a material with a uranium isotopic composition comparable to SRM A (approximately 20% ^{235}U), we also analyzed two samples of SRM U-200 by the same procedures.

Results for the internal-standard measurement of the $^{235}\text{U}/^{238}\text{U}$ atom ratio in duplicate runs for the three SRM A samples designated for isotopic analysis are shown in Table 6.

Table 6. Results of Internal-Standard Measurement of $^{235}\text{U}/^{238}\text{U}$ Atom Ratio in SRM A Samples.

Sample No.	Measured $^{235}\text{U}/^{238}\text{U}$ Atom Ratios		
	Run #1	Run #2	Average
A-97	0.2513374	0.2513678	0.2513526
A-179	0.2513482	0.2513415	0.2513448
A-199	0.2513530	0.2513624	0.2513577
Average			0.2513517
Std. Dev.			± 0.0000065
RSD			$\pm 0.0026\%$

The relative standard deviation of these measurements, 0.0026% on the three means of the two measurements, is typical of the precision achievable with the internal-standard approach to determining a ratio of major isotopes and demonstrates uniform isotopic composition among the SRM A pellets.

Having established a value for the ratio of major isotopes in the SRM A uranium, we used this value to evaluate fractionation corrections for separate isotopic measurements on samples where the internal standard spike was not added, and we applied these corrections to ratios obtained for the minor isotopes in each measurement run. Results of these measurements are summarized in Table 7, which shows values obtained for the major and minor isotope ratios, both before and after the ratios were normalized to the average $^{235}\text{U}/^{238}\text{U}$ value from Table 6.

The internal normalization procedure did not substantially improve the precision of the minor isotope ratio values obtained from the measurements in Table 7. This is because the measurement precision for these small ratios is controlled by signal noise and baseline variation in the mass spectrometer detection system and not by variations in the fractionation pattern for the isotopes, as

Table 7. Results of Minor Isotope Measurements for SRM A Uranium before and after Normalization to $^{235}\text{U}/^{238}\text{U}$ Ratio from Internal-Standard Runs.

Sample No.	Run No.	Measured Atom Ratio of Uranium Isotopes			Corrected Atom Ratio of Uranium Isotopes		
		234/238	236/238	235/238	234/238	236/238	235/238
A-97	1	0.0014134	0.0017352	0.2510544	0.0014156	0.0017366	0.2513517
	2	0.0014191	0.0017367	0.2511874	0.0014203	0.0017375	0.2513517
	Avg.	0.0014162	0.0017360	0.2511209	0.0014180	0.0017370	0.2513517
A-179	1	0.0014157	0.0017350	0.2511286	0.0014174	0.0017360	0.2513517
	2	0.0014212	0.0017386	0.2513446	0.0014212	0.0017386	0.2513517
	Avg.	0.0014184	0.0017368	0.2512366	0.0014193	0.0017373	0.2513517
A-199	1	0.0014172	0.0017362	0.2508795	0.0014208	0.0017384	0.2513517
	2	0.0014200	0.0017388	0.2509906	0.0014227	0.0017405	0.2513517
	Avg.	0.0014186	0.0017375	0.2509350	0.0014218	0.0017394	0.2513517
Avg. (Six Runs)		0.0014178	0.0017367	0.2510975	0.0014197	0.0017379	0.2513517
Std. Dev. (Six Runs)		0.0000029	0.0000016	0.0001618	0.0000026	0.0000016	--
RSD (Six Runs)		0.205%	0.094%	0.064%	0.186%	0.093%	--

is the case for ratios involving larger signals, where the signal noise contributes small variability relative to fractionation effects. For the analysis runs where a conventional "external" fractionation correction is applied, weakness of the external correction procedure shows itself in the measured $^{235}\text{U}/^{238}\text{U}$ ratio, for which we find poorer precision than when the internal standard is used (compare Tables 6 and 7) and a bias between the average $^{235}\text{U}/^{238}\text{U}$ ratio measured by the two approaches. This bias (approximately 0.10%, relative, in the value for the ratio) derives from the practical difficulty of reproducing analysis conditions between runs with the calibration standard and runs with the samples being analyzed. With the internal normalization approach applied in this work, sample-to-sample differences in loading and analysis are compensated for in a way that minimizes this potential for bias in the measurement results.

To assess the magnitude of residual bias in the isotope ratios determined with the internal standard/internal normalization approach that was applied to the SRM A uranium samples, we applied the same approach to analyzing the Standard Reference Materials U-500 and U-200. Results of the internal-standard measurements of the $^{235}\text{U}/^{238}\text{U}$ ratio in four analyses of U-500 and two analyses of U-200 are shown in Table 8.

Table 8. Results of Internal-Standard Measurements of $^{235}\text{U}/^{238}\text{U}$ Atom Ratio in Standard Reference Materials U-500 and U-200.

Run No.	Measured $^{235}\text{U}/^{238}\text{U}$ Atom Ratios	
	U-500	U-200
1	0.9995914	0.2511744
2	0.9997714	0.2511830
3	0.9997108	--
4	0.9996909	--
Average	0.9996911	0.2511787
Std. Dev.	0.0000075	0.0000061
RSD	0.0075%	0.0024%
NBS Value	0.9997 ± 0.0010	0.25126 ± 0.00025
Difference from NBS	0.0000089	0.000081
Rel. Diff. from NBS	0.00089%	0.032%

These results demonstrate the absence of residual bias relative to the ratio of major isotopes in SRM U-500, which was the designated reference material for isotopic analysis of the SRM A uranium. The average of $^{235}\text{U}/^{238}\text{U}$ ratios measured with the internal standard procedure differs from the reference value by less than one part in 100,000; this observation confirms the validity of the calibration of the internal standard spike, which was calibrated with the U-500 reference

material and should, therefore, reproduce the U-500 reference value in a test such as this. In the case of the U-200 reference material, a small bias (0.032%, relative) is observed for the $^{235}\text{U}/^{238}\text{U}$ ratio. This difference between the measured and reference values for this ratio is smaller than the uncertainty in the reference value and might reflect a real difference between the U-500 and U-200 certification bases rather than a deficiency in the measured values. Nevertheless, in assigning uncertainties to the measured isotope ratios for the SRM A uranium, we include a term to allow for a possible bias in the $^{235}\text{U}/^{238}\text{U}$ isotope ratio of 0.032%, as observed for the U-200 standard.

Results from determination of the minor isotope ratios in the U-500 and U-200 reference materials, with internal normalization to the major isotope ratio, are summarized in Table 9. The ratios obtained for uranium isotopes in the U-500 and U-200 reference materials are compared with the NBS certificate values in Table 10. Small differences between the measured and certified values for the minor isotopes in each reference material are apparent, which might reflect bias error from nonlinearity of the mass spectrometer measuring systems or baseline-correction deficiencies in the measurements made in determining these small ratios. Because none of the observed differences exceeds the combined uncertainties of the measured and certified values, the evidence is not compelling that any real bias actually exists. To account for the possibility of such bias, however, we have included a term in the uncertainty estimate we apply for SRM A uranium isotope ratios that is equal to the largest difference observed between the measured and certified ratios of magnitude comparable to the minor isotope ratios in SRM A. This term, which has a magnitude of 0.000007 as determined from the 236/238 ratio in SRM U-200, is added to terms from other potential error sources in assigning uncertainties to the SRM A isotope ratios.

Calculation of atom and weight percent abundances of the uranium isotopes in SRM A is summarized in Table 11. The measured atom ratios of individual isotopes to ^{238}U are listed in this table together with an uncertainty for each measured ratio. Each uncertainty was calculated as the sum of three terms. The first term represented the 95% confidence interval half-width for the mean of the six measured values for the listed ratio as given by $t \cdot s / \sqrt{N}$, where t is the Student's t -value for $\alpha = 0.05$ and five degrees of freedom; s is the standard deviation of the measured values (Table 6 or Table 7); and $N = 6$ is the number of measurements included in determining the average value. The second term represented a potential for bias in applying fractionation corrections based on U-500 to materials having a different ratio of major isotopes; the value of this term was calculated as 0.032% of each ratio on the basis of the difference between measured and certified values for $^{235}\text{U}/^{238}\text{U}$ in U-200. The third term represented a potential for bias from deficiencies in linearity corrections or baseline corrections during measurement of small ratios (<0.003); the value of this term was set to 0.000007 for every ratio on the basis of values observed for the minor isotopes in the U-500 and U-200 standards. Generally, the terms representing potential bias in the reported ratio contribute the greatest uncertainty to the reported value. This reflects the high precision obtained with the internal-standard/internal-normalization approach taken in the isotopic analysis for SRM A and the difficulty of assessing small biases in the absence of reference materials certified to a level of uncertainty comparable to that of the measurements being made.

Table 9. Results of Minor Isotope Measurements for Standard Reference Materials U-500 and U-200 before and after Normalization to $^{235}\text{U}/^{238}\text{U}$ Ratio from Internal-Standard Runs.

Sample No.	Run No.	Measured Atom Ratios of Uranium Isotopes			Corrected Atom Ratios of Uranium Isotopes		
		234/238	236/238	235/238	234/238	236/238	235/238
U-500	1	0.0103984	0.0015132	0.9987255	0.0104118	0.0015142	0.9996911
	2	0.0103933	0.0015138	0.9986739	0.0104074	0.0015148	0.9996911
	3	0.0104104	0.0015241	0.9994923	0.0104132	0.0015243	0.9996911
	4	0.0103861	0.0015146	0.9989834	0.0103959	0.0015153	0.9996911
	5	0.0104038	0.0015211	0.9992623	0.0104098	0.0015215	0.9996911
Average		0.0103984	0.0015174	0.9990275	0.0104076	0.0015180	0.9996911
Std. Dev.		0.0000094	0.0000049	0.0003498	0.0000069	0.0000046	--
RSD		0.090%	0.324%	0.035%	0.066%	0.302%	--
U-200	1	0.0015535	0.0026487	0.2506827	0.0015576	0.0026522	0.2511787
	2	0.0015588	0.0026448	0.2509915	0.0015604	0.0026461	0.2511787
Average		0.0015562	0.0026468	0.2508371	0.0015590	0.0026492	0.2511787
Std. Dev.		0.0000037	0.0000028	0.0002184	0.0000020	0.0000043	--
RSD		0.241%	0.104%	0.087%	0.127%	0.163%	--

Table 10. Comparison of Measured and Certified Values for Uranium Isotope Ratios in U-500 and U-200 Standard Reference Materials.

Reference Material	Data Source	Atom Ratios		
		234/238	235/238	236/238
U-500	Measured	0.0104076 $\pm 0.0000086^a$	0.9996911 $\pm 0.0000119^a$	0.0015180 $\pm 0.0000057^a$
	Certificate	0.010422 ± 0.000016	0.9997 ± 0.0010	0.001519 ± 0.000006
	Measured – Certificate	-0.000014 ₄ (0.14%)	-0.0000089 (0.0009%)	-0.000001 ₀ (0.066%)
U-200	Measured	0.0015590 $\pm 0.0000180^a$	0.2511787 $\pm 0.0000548^a$	0.0026492 $\pm 0.0000386^a$
	Certificate	0.001564 ± 0.000004	0.25126 ± 0.00025	0.002656 ± 0.000008
	Measured – Certificate	-0.000005 ₀ (0.32%)	-0.000008 ₁ (0.032%)	-0.000006 ₈ (0.26%)

^aUncertainty calculated as 95% confidence interval half-width for measured value; given by $ts/\sqrt{N}$, where t is the Student's t value for N measurements, and s is the standard deviation of the measured value from Table 8 or Table 9.

Table 11. Atom and Weight Percent Abundances of Uranium Isotopes in SRM A Uranium.

A. Input Data				
	234/238	235/238	236/238	238/238
Atom Ratios ^a	0.0014197 ± 0.0000096	0.2513517 ± 0.0000939	0.0017397 ± 0.0000089	1.000...
Weight Ratios ^b	0.0013958 ± 0.0000094	0.2481768 ± 0.0000927	0.0017233 ± 0.0000088	1.000...
B. Isotopic Abundances				
	²³⁴ U	²³⁵ U	²³⁶ U	²³⁸ U
Atom Percent	0.1132 ± 0.0006	20.0358 ± 0.0060	0.1385 ± 0.0006	79.7124 ± 0.0057
Weight Percent	0.1115 ± 0.0006	19.8336 ± 0.0059	0.1377 ± 0.0006	79.9171 ± 0.0057

^aAverage values of measured atom ratios from Table 6 or Table 7.

^bProduct of atom ratio and corresponding ratio of nuclidic masses using the following mass values: ²³⁴U = 234.0409; ²³⁵U = 235.0439; ²³⁶U = 236.0456; ²³⁸U = 238.0508 (from Chart of the Nuclides, General Electric Co., April 1988).

Atom percent abundances of the uranium isotopes in SRM A were calculated from the measured atom ratios and the relationship

$$(Atom\ \%)_i = \frac{100\% R_i}{\sum R_j}, j = 234, 235, 236, 238 \quad (1)$$

where R_i is the atom ratio of isotope i to ^{238}U . Note that the value of R_{238} in this expression is equal to unity and is included in the summation in the denominator on the right side of Eq. 1. The uncertainty in each atom percent abundance value was estimated by propagating the uncertainties in the individual ratios through the formula in Eq. 1. The expression employed for estimating these uncertainties is

$$\Delta(Atom\ \%)_i = (Atom\ \%)_i \cdot \frac{(Atom\ \%)_{238}}{100} \cdot (\Delta R_i/R_i + \sum \Delta R_j/\sum R_j), i \neq j \quad (2)$$

where $\Delta(Atom\ \%)_i$ is the uncertainty in $(Atom\ \%)_i$ and ΔR_i is the uncertainty in the ratio R_i . Weight percent abundances of the uranium isotopes were calculated in an analogous manner, with weight ratios derived from the measured atom ratios and ratios of the nuclidic masses of the corresponding isotopes. Values for the nuclidic masses were taken from the "Chart of the Nuclides" prepared by General Electric Co. (April 1988).

B. Uranium Concentration in SRM A

As described in Sec. IV.B.2, duplicate aliquots of the solution obtained from each SRM A salt pellet were separately diluted and spiked with CRM-111A ^{233}U to provide samples for assay of the SRM A uranium by MSID. Each of the samples in these ten pairs of duplicates was analyzed by TIMS, using the internal standard procedure, to determine the $^{235}\text{U}/^{233}\text{U}$ and $^{238}\text{U}/^{233}\text{U}$ ratios in the sample/spike mixture. From these ratios, the quantity of uranium in the aliquot of solution taken from the dissolved SRM pellet was calculated, and the weight percent uranium in the pellet from which each aliquot came was obtained by relating the aliquot weight to the total solution mass and pellet mass.

Isotope dilution assay is based on the precept that each ratio of isotopes in a mixture of isotopically different materials is related to the isotope abundances in each material and the relative quantities of each material in the mixture. Thus, if the isotopic composition of two materials is known and the quantity of one of the materials in the mixture is available, the quantity of the second material in the mixture can be computed from the isotopic composition of the mixture. In the case of the SRM A uranium assays, we looked at the ratio of ^{238}U to ^{233}U in the mixture because these are the most abundant isotopes in the unknown uranium (SRM A) and spike uranium (CRM-111A). The observed mass ratio of ^{238}U to ^{233}U in the sample/spike mixture can be related to the isotope abundances and quantities of the unknown uranium and spike uranium, as shown in Eq. 3:

$$R_{8/3} = \frac{m_u \cdot {}^8f_u + m_s \cdot {}^8f_s}{m_s \cdot {}^3f_s} \quad (3)$$

In Eq. 3, $R_{8/3}$ is the measured mass ratio of ^{238}U to ^{233}U in the spike/sample mix; m_u is the mass of unknown uranium in the mixture; m_s is the mass of spike uranium present in the mixture and is known from the prepared value for the spike; and f_j is the mass fraction abundance of isotope i in material j (where $j = s$ for spike or $j = u$ for unknown). When the ratio $R_{8/3}$ is measured, values for all the parameters in Eq. 3 are available, except for m_u , which can be evaluated by solving the equation. By rearranging Eq. 3, the solution for m_u can be expressed as

$$m_u = m_s \cdot \frac{R_{8/3} \cdot {}^3f_s - {}^8f_s}{{}^8f_u} \quad (4)$$

An analogous relationship can be derived between m_u and parameters related to ^{235}U in the SRM A and spike uranium. We also computed m_u for each spiked sample using the measured $^{235}\text{U}/^{233}\text{U}$ ratio, as a check for consistency in our isotopic measurements and as a way to test for inadvertent contamination of a given sample with uranium from a source other than the SRM A material or the CRM-111A spike.

For our isotope dilution calculations, we used the weight percent abundances of ^{238}U (79.9171%) and ^{235}U (19.8336%) as shown in Table 11 for the SRM A uranium. Values for weight-percent abundances of the isotopes in CRM-111A were derived from the atom percent abundances on the NBL certificate. These derived values were 99.4845% for ^{233}U , 0.07967% for ^{235}U , and 0.2335% for ^{238}U .

Weight percent concentrations for uranium in each SRM A pellet were calculated from the m_u results, the masses of aliquots taken and dilutions made, and the mass of the pellet that was dissolved. The formula used for these calculations is

$$C_u = \frac{m_u \cdot M_{DISS} \cdot M_{DIL} \cdot 100\%}{M_{ALQDISS} \cdot M_{ALQDIL} \cdot M_{Pellet}} \quad (5)$$

In Eq. 5, C_u is the weight percent concentration of uranium in the SRM A pellet; m_u is the mass of uranium in the spiked solution aliquot as determined by MSID and Eq. 4; M_{DISS} is the mass of the original pellet solution; M_{DIL} is the total mass of the diluted sample solution aliquot; $M_{ALQDISS}$ is the mass of the original pellet solution aliquot that was diluted; M_{ALQDIL} is the mass of the diluted solution aliquot added to the spike beaker; and M_{Pellet} is the mass of the SRM A unit that was dissolved.

Results of the SRM A unit uranium assays are summarized in Table 12 for the ten salt pellets that were analyzed in our characterization of the uranium concentration. In this table, we show the unit identification, the measured mass of the unit that was dissolved, and the values for the individual uranium concentrations determined from each spiked sample using either the $^{235}\text{U}/^{233}\text{U}$ ratio in the spike/sample mixture or the $^{238}\text{U}/^{233}\text{U}$ ratio. Before compiling these data, we performed brief statistical analyses to compare results obtained from each of the two groups of five units that were analyzed together and to look for evidence of any gradual concentration changes in the units as a function of when a given unit was poured. A Student's t-test comparison of the means of the two groups of five samples indicated (at the 95% confidence level) that the mean of the first group of units (2.5073 wt. % U) is significantly different from the mean of the second group (2.5043 wt. % U), despite this difference corresponding to only 0.12% of the SRM uranium concentration. Because the number of samples in each group is small, and because the combined data from the two groups showed a normal distribution with no evidence of bimodality, we chose to ignore this difference in our further treatment of the data. Regression analysis of the measured uranium concentration in a given unit as a function of the unit sequence number showed a weak correlation between the uranium concentration and order of pouring (correlation coefficient of 0.70). Using the regression formula to model the uranium concentration in a given unit did not, however, reduce the residual variance of the system. Thus, this analysis did not produce evidence of systematic variations in the SRM uranium concentration. In light of these preliminary data evaluations, results from all ten units were taken to represent a single, normally distributed population in the data analysis. The results are treated in the context of this model in the following discussion.

In general, agreement is excellent between the concentration calculated from the $^{235}\text{U}/^{233}\text{U}$ ratio and that calculated from the $^{238}\text{U}/^{233}\text{U}$ ratio for each individual spiked sample. This observation argues against inadvertent contamination of these samples by uranium of different isotopic composition than the sample or spike. One exception to this general observation occurs for one of the duplicate measurements with the A-179 unit, where widely different results were obtained from calculations based on ^{235}U and those based on ^{238}U . This difference and the exceptionally high concentration values for this sample provide a strong indication that this sample was contaminated with extraneous uranium of much lower ^{235}U enrichment than that present in SRM A. The results from this sample were, therefore, not included in our processing of the uranium assay data to compute averages or standard deviations.

On average, agreement between values computed from the measured $^{235}\text{U}/^{233}\text{U}$ ratios and those from the $^{238}\text{U}/^{233}\text{U}$ ratios is remarkably consistent, with the average concentrations over all units showing a difference of approximately 2 parts in 25,000. Given this consistency, we opted to use a simple average of the results from the two ratios as the value of the weight percent U from each determination performed

Table 12. Uranium Assay Results for SRM A Units Analyzed by Mass Spectrometric Isotope Dilution.

SRM A Unit	Unit Mass, g	Wt. % U from $^{235}\text{U}/^{233}\text{U}^{\text{a}}$	Wt. % U from $^{238}\text{U}/^{233}\text{U}^{\text{b}}$	Wt. % U for Sample ^c	Wt. % U for Unit ^d
A-14 ^e	1.0952 ₅	2.50285 2.50388	2.50308 2.50364	2.50296 2.50376	2.50336
A-34 ^e	1.1716 ₀	2.50483 2.50377	2.50528 2.50413	2.50506 2.50395	2.50450
A-53 ^e	1.0801 ₀	2.50177 2.50158	2.50205 2.50152	2.50191 2.50155	2.50173
A-73 ^e	1.1931 ₁	2.50486 2.50665	2.50464 2.50702	2.50475 2.50684	2.50579
A-97 ^f	1.1385 ₅	2.50750 2.50806	2.50766 2.50803	2.50758 2.50804	2.50781
A-117 ^f	1.1198 ₃	2.50800 2.50366	2.50645 2.50450	2.50722 2.50408	2.50565
A-137 ^f	1.1852 ₀	2.50530 2.50594	2.50572 2.50712	2.50551 2.50653	2.50602
A-157 ^f	1.0741 ₀	2.50912 2.50637	2.50926 2.50718	2.50919 2.50678	2.50798
A-179 ^f	1.2873 ₀	2.50834 2.51003 ^g	2.50971 2.52107 ^g	2.50902 2.51555 ^g	2.50902
A-199 ^e	2.0922 ₅	2.50727 2.50538	2.50664 2.50524	2.50696 2.50531	2.50613
	Average	2.50553	2.50573	2.50563	2.50580
	Std. Dev.	0.00223	0.00227	0.00223	0.00220

^aValues calculated from $^{235}\text{U}/^{233}\text{U}$ mass ratio measured for spiked samples.

^bValues calculated from $^{238}\text{U}/^{233}\text{U}$ mass ratio measured for spiked samples.

^cAverage of values calculated from ^{235}U and ^{238}U in previous columns; pooled RSD of duplicate pairs is 0.0480% (A-179 excluded).

^dAverage of duplicate values for corresponding unit; only one value for A-179.

^eUnit was part of second group of five samples processed for analysis.

^fUnit was part of first group of five samples processed for analysis.

^gValues indicate contamination with extraneous uranium; data not included in averages or standard deviation.

with a particular sample aliquot. Then, we averaged the results from aliquots corresponding to a given SRM A unit to obtain the value for the weight percent U in that unit, as shown in the last column of Table 12. These results show an average uranium concentration of 2.50580 wt. %, with a standard deviation over the 10 pellets of 0.00220 wt. % (0.0878%, relative).

In designing the sampling and analysis plan for the SRM A characterization, we included replicate measurements that would permit an assessment of the uniformity of the SRM batch in addition to a reference value for the uranium concentration. This design was based on a model for the variance of the measured values, in which the observed variance of the pellet analyses, σ_{OBS}^2 , is composed of variance contributions from three sources: (1) variance associated with determining the pellet mass, $\sigma_{M_{Pellet}}^2$; (2) variance in the MSID measurement of uranium in the solution prepared by dissolving the pellet, σ_{MSID}^2 ; and (3) variance arising from pellet-to-pellet differences in uranium content, σ_{Units}^2 . This model is described by the relationship

$$\sigma_{OBS}^2 = \sigma_{M_{Pellet}}^2 + \sigma_{MSID}^2 / 2 + \sigma_{Units}^2 \quad (6)$$

The factor of two divisor in the term corresponding to σ_{MSID}^2 accounts for the use of duplicate aliquots in the MSID measurements for each pellet.

An assessment of nonuniformity among the SRM A units corresponds to estimating a value for σ_{Units}^2 and determining whether the magnitude of this variance is significant relative to the other terms in Eq. 6. To estimate σ_{Units}^2 , we first rearrange Eq. 6 to obtain Eq. 7, and then evaluate the individual terms needed to solve for the desired variance:

$$\sigma_{Units}^2 = \sigma_{OBS}^2 - \sigma_{MSID}^2 / 2 - \sigma_{M_{Pellet}}^2 \quad (7)$$

Values for σ_{OBS}^2 and σ_{MSID}^2 are available from the data in Table 12. For σ_{OBS}^2 , the RSD of the results from the 10 pellets that were analyzed gives the value $(0.0878\%)^2$. For σ_{MSID}^2 , the pooled RSD of the nine duplicate pairs of MSID measurements gives a value of $(0.0480\%)^2$. Because each pellet could be weighed and dissolved only once, the variance associated with determining the pellet mass could not be determined from replicate operations. Consequently, we estimate the variance of determining the pellet mass from the variance observed during our weighing of standard masses to test the balance performance (see Table 5). In those tests, we found that a single weighing with the balance we employed could be assigned a standard deviation of 0.00016 g. Because each pellet mass was determined as the difference between two measured masses (i.e., bottle-plus-pellet minus bottle tare), we assign a value of $2 \times (0.00016 \text{ g})^2$ to the weighing variance. To put the weighing variance on the same RSD basis as the other terms in Eq. 7, we further divide the weighing standard deviation by the mass of a typical pellet (as a conservative and convenient approximation, a mass of 1 g was used) and multiply by 100% to obtain a value for $\sigma_{M_{Pellet}}^2$ of $(0.0226\%)^2$.

Substituting the appropriate values into Eq. 7, we obtain

$$\sigma_{Units}^2 = (0.0878\%)^2 - (0.0480\%)^2/2 - (0.0226\%)^2 = (0.0778\%)^2 \quad (8)$$

which provides the value $(0.0778\%)^2$ for σ_{Units}^2 . Regardless of which statistical test of significance one might apply, this value is a clearly significant contributor to the observed pellet-to-pellet variations in the measured values and demonstrates a probable nonuniformity in the SRM A units. This nonuniformity must be considered in applying the SRM for quality control and process characterization and is treated in our later discussion of reference values for the SRM A uranium concentration.

The cause of this apparent nonuniformity of the pellets is difficult to identify. One possibility that we can point to, however, relates to operations in the dispensing of the SRM A units, wherein some fraying of insulation on the dispensing apparatus was noted. If small particles of frayed insulation were introduced at random into the poured units, the apparent uranium content relative to the unit mass would be changed. The observed level of nonuniformity (0.0778%) would correspond to a distribution of contamination levels for different units of less than 0.8 mg of contaminant per gram of poured salt. Such quantities of material would be very difficult to observe or control in a glovebox environment and might be a credible source of the apparent variations in uranium concentration that we see among the units.

From the average of the 10 units analyzed, our best estimate of the mean concentration of uranium in the SRM A salt samples is 2.5058 wt. %. Uncertainty in this mean value arises from random effects, which were briefly described above, and from systematic effects (biases) that influence the results for each unit in the same way and have to be evaluated from consideration of the operations, standards employed, and other factors. By examining the formulas from which each assay result was computed, we identified the following potential bias sources.

a. Bias in the mass of spike uranium, m_s . The NBL certificate for the CRM-111A spike material lists a uranium concentration uncertainty equivalent to $\pm 0.025\%$ of the certified uranium content. This uncertainty could be used to assign a limit to potential bias from the spike in our measurements. However, when we tested our prepared spike stock solution with NBS 950a uranium, we observed a somewhat larger bias of $0.061 \pm 0.065\%$, relative (see Sec. IV.A). If we interpret this observation to indicate that the uranium content of our prepared spikes was actually smaller than the value calculated from the NBL concentration, our reported uranium assay results would be too high by $0.061 \pm 0.065\%$. In contrast, if we interpret the observed difference as a bias in our measurements, the assay results would be too low by $0.061 \pm 0.065\%$. Since we have no way to determine from the data at hand which case applies, the limit to potential bias from this source was set at $\pm 0.127\%$, relative, which is the maximum value of the potential error in either direction (i.e., $\pm 0.061\% \pm 0.065\%$).

b. Bias in the measured ratio of sample to spike isotopes, R_{ij} . Since the isotope ratios for the MSID assays were measured with the internal-standard procedure, this bias contribution is considered negligible.

c. Bias in the abundances of the sample and spike isotopes, 3f_s , 8f_u , 8f_s . Any errors in the isotopic abundance values used in the MSID calculations would also translate to a bias in the calculated assay result. From differences between our isotopic results for CRM-111A and the NBL certificate, we assigned a limit to potential bias from the spike isotopes of $\pm 0.01\%$, relative. From uncertainties assigned to our measurements of the isotopic composition of the SRM A uranium, we assign a limit to bias from the ^{238}U isotopic abundance of $\pm 0.007\%$, relative. Other potential errors from isotope abundance uncertainties were taken as negligible relative to these.

d. Bias from measuring masses of solutions and pellets, M_{Pellet} , etc. During our balance performance tests, we identified a potential bias of $+0.3$ mg in each mass measurement. However, because all object masses measured during the assay operations were determined by difference, any such bias would be expected to cancel when the object mass was calculated. Hence, bias from the measured masses need not be considered in estimating the assay uncertainty.

To assign a limit to potential bias in the uranium assay results for SRM A, we elected to sum the individual limits to relative bias error, $^B\text{Limit}_a$, $^B\text{Limit}_b$, $^B\text{Limit}_c$, and $^B\text{Limit}_d$, identified for sources a, b, c, and d listed above. Thus, the limit to potential bias, $^B\text{Limit}$, is given by

$$\begin{aligned} B_{\text{Limit}} &= B_{\text{Limit}_a} + B_{\text{Limit}_b} + B_{\text{Limit}_c} + B_{\text{Limit}_d} \\ &= \pm 0.127\% \pm 0\% \pm 0.017\% \pm 0\% \\ &= \pm 0.144\% \end{aligned} \quad (9)$$

With values determined for the mean of the MSID assay results, the estimates of variances associated with individual random effects, and the estimate of the magnitude of potential systematic effects, we may develop a description of the SRM A uranium concentration that will establish limits within which the concentration might be expected to fall with specific levels of confidence. Because of the observed unit-to-unit variation in the apparent uranium concentration in the SRM A units, two cases need to be addressed in this treatment. The first case involves establishing the interval in which the mean uranium concentration of the SRM A unit batch will fall if all units are analyzed. This case may be considered to establish the reference value for measurement of multiple units of the SRM A material. The second case involves establishing the interval in which the uranium concentration of any individual unit might fall; it is important to establishing control limits for measurement processes in which the SRM A units might be applied, since method performance cannot be evaluated at a level better than the quality of the reference material used in the method assessment.

For the first case, the confidence interval about the average measured uranium concentration is given by the relationship,

$$CI_{\text{Mean}} = \bar{x} \pm t_{N-1} \cdot s/\sqrt{N} \pm B_{\text{Limit}_{\text{ABS}}} \quad (10)$$

where CI_{Mean} is the interval in which the mean value of the concentration is expected to fall; $\bar{x}$ is the average of the measured values; t_{N-1} is the Student's t parameter for $N-1$ degrees of freedom and a selected confidence level; s is the standard deviation of the measured values estimated from N measurements; and B_{Limit_ABS} is the limit to probable bias expressed on an absolute basis (i.e., as opposed to a relative basis). Taking the ten measurements in Table 12 as the pertinent data set, selecting the t value for 9 degrees of freedom and a 95% confidence level ($t = 2.26$), and using the value $\pm 0.144 \bar{x} / 100$ for B_{Limit_ABS} , this interval is given, in units of weight percent, by

$$CI_{Mean} = 2.50580 \pm (2.26) (0.00220) / \sqrt{10} \pm 0.00361 \quad (11)$$

or

$$CI_{Mean} = 2.50580 \pm 0.00518 \text{ wt. \% } U \quad (12)$$

For the second case mentioned above, i.e., the interval in which the uranium concentration of any individual SRM unit might be expected to fall, we extend the interval in Eq. 12 by an amount determined as $t_{N-1} \cdot s_{Units}$, where s_{Units} is the estimate of σ_{Units} obtained from the data treatment presented earlier ($s_{Units} = 0.0778\%$, relative, which corresponds to 0.00195 wt. %, absolute). Thus, the interval in which the uranium concentration of 95% of the individual SRM units might be expected to fall, CI_{Indiv} , is given by

$$\begin{aligned} CI_{Indiv} &= 2.50580 \pm 0.00518 \pm 2.26 \cdot (0.00195) \text{ wt. \% } U \\ &= 2.50580 \pm 0.00959 \text{ wt. \% } U \end{aligned} \quad (13)$$

VI. SUMMARY AND CONCLUSIONS

Isotopic analysis and MSID assay of uranium in selected SRM A units have provided reference values for the uranium isotope abundances and for the uranium concentration in the batch of LiCl/KCl portions that comprise the Special Reference Material. The isotopic composition of uranium in the batch appears uniform within the precision of measurements made with an exceptionally precise, internal-standard procedure applied in TIMS measurements by the ANL-E Analytical Chemistry Laboratory.

Results obtained from MSID assays on ten SRM units indicate that the apparent uranium concentration (wt. % U) is not uniform over the batch of units but exhibits a distribution of values having an estimated standard deviation of 0.078%, relative (0.00195 wt. %, absolute). Thus, although the MSID assays showed a precision of approximately 0.053% RSD (estimated by combining the pooled RSD from duplicate measurements with an estimated RSD for determining the mass of each unit), the mean concentration of uranium in this SRM batch could not be determined with a corresponding small level of certainty. Taking into account uncertainty contributions from both random and potential systematic effects that might have influenced our results, the mean value for the SRM A uranium concentration is expected to lie within the interval 2.5058 ± 0.0052 wt. %. Because of the unit-to-unit differences in apparent uranium concentration that are seen in our data, uranium concentration values for individual units may be expected to fall outside this interval, but they are anticipated to fall in the range 2.5058 ± 0.0096 wt. % U.

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