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NBS SPECIAL PUBLICATION 260-27

Standard Reference Materials:

URANIUM ISOTOPIC STANDARD REFERENCE MATERIALS

U.S.
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UNITED STATES DEPARTMENT OF COMMERCE • Maurice H. Stans, *Secretary*
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, *Director*

Standard Reference Materials:

Uranium Isotopic Standard Reference Materials

(Certification of Uranium Isotopic Standard Reference Materials)

E. L. Garner, L. A. Machlan, and W. R. Shields

Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

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PREFACE

Standard Reference Materials (SRMs) as defined by the National Bureau of Standards are "well-characterized materials, produced in quantity, that calibrate a measurement system to assure compatability of measurement in the nation." SRMs are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. In many industries traceability of their quality control process to the national measurement system is carried out through the mechanism and use of SRMs. For many of the nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRMs produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on all phases of the preparation, measurement, and certification of NBS-SRMs. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. It is also hoped that these papers will provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

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E. L. Garner, L. A. Machlan and W. R. Shields

Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

An ignition procedure has been developed that will yield reproducible stoichiometry for U_3O_8. The effects of temperature, length of ignition, rate of cooling, pressure and type of atmosphere were investigated. This ignition procedure has been used for the blending of high purity ^{235}U and ^{238}U separated isotopes to prepare calibration standards for the determination of bias effects in the thermal emission mass spectrometry of uranium. Weight aliquoting was used to prepare calibration mixes with ^{235}U/^{238}U ratios of more than 10 and less than 0.1 and to add a ^{233}U spike for the determination of minor isotope abundances in the uranium isotopic standards by the isotope dilution technique.

A description of the unique features of the mass spectrometer instrumentation including the source, NBS collector and expanded scale recorder are given. Two specific analytical procedures were used for the isotopic analysis of uranium and are adaptable, within a general framework, to fit the particular ion current intensity requirements of a wide range of isotopic distributions. Mass discrimination due to evaporation and ionization on the filaments, and other parameters such as temperature, time, sample size, sample mounting, total sample composition, acidity, filament material, pressure, non-ohmic response, R-C response and source memory were studied as part of the development effort to establish sound analytical procedures.

The absolute isotopic abundances of 18 uranium SRMs were determined by thermal emission mass spectrometry. The general approach was to determine absolute ^{235}U/^{238}U ratios by using calibration mixes to correct for filament bias. Then the absolute ^{234}U and ^{236}U were determined by ^{233}U isotope dilution. For SRM U-0002, isotope dilution was the only practical means of determining the low abundance of ^{235}U as well as the ^{234}U. The limits given for the isotopic composition of the uranium SRMs are at least as large as the 95 percent confidence limits for a single determination and include terms for inhomogeneities of the material as well as analytical error.

Key words: Absolute isotopic abundance; ignition procedure; isotopic standards, mass spectrometry; stoichiometry; uranium.

1. INTRODUCTION

This publication describes the work by the Analytical Mass Spectrometry Section of the National Bureau of Standards on the development and characterization of standard reference materials for the isotopic composition of uranium.

The initial measurement of the isotopic composition of uranium Standard Reference Materials (SRMs) was completed in 1959 with 95 percent confidence limits of 0.5 percent for the least abundant of the major isotopes (^{235}U and ^{238}U) and above one percent for the minor isotopes (^{234}U and ^{236}U). A 5 year period of intensive evaluation and development of the chemical procedure, the mass spectrometric instrumentation and the mass spectrometric analytical procedure followed this initial effort. The SRMs played a unique and dual role of providing a group of high purity working standards to develope methods to analyze uranium, and also to provide a uniform set of standards with a wide range of isotopic abundances to evaluate, develop and improve the mass spectrometric instrumentation. Informational fallout from the development of a uranium analytical method was beneficial and applicable to the analysis of other elements. It was demonstrated that many of the general rules and control procedures necessary to make a meaningful comparison of ion currents were basically the same and were independent of the elemental ions measured.

The complete analytical method for any isotopic measurement is divisible into three broad areas; chemistry, instrumentation and mass spectrometric procedure. A prerequisite for an accurate isotopic measurement is an evaluation of the error contributions from each of these sources. Since any of these can cause a serious loss of precision and accuracy, equal attention must be given to all phases of the measurement.

2. CHEMISTRY

A. Introduction

The chemistry requirements in the characterization of these standards were the accurate blending of separated isotopes to provide standards for mass spectrometer calibration and the accurate additions of "U233" separated isotope for the isotope dilution determinations of the minor isotopes. In addition it was necessary to provide solutions that were uniform in uranium and acid concentrations, and that were very low in impurities.

B. Ignition of U_3O_8

The goal of the early investigation was to find an ignition procedure that would give a reproducible stoichiometry for U_3O_8 irrespective of the previous history of the starting materials. If a reproducible oxide could be produced, weighed portions of the high purity "U235" and "U238" separated isotopes could be blended directly or aliquots taken to prepare accurately known mixes for the mass spectrometer calibration. Even if the ignited samples of U_3O_8 were not stoichiometric, as long as the oxides were both nonstoichiometric to the same degree, the blending would produce the same isotopic composition as stoichiometric oxides. The same criteria also applied to the ^{233}U isotope dilution for the minor isotope determinations. Previous work on the certification of uranium oxide (U_3O_8) assay standards, SRMs 950 and 950a, indicated a difference of about 0.06 percent between the assay and the value calculated from impurity determination. This difference was considered to represent deviations from the nominal stoichiometric composition. The assay, 99.94 percent, was based on material ignited at 900 °C for one hour in an open crucible and cooled in a desiccator.

The ignitions in this investigation were conducted in a tube furnace. In a comparison with the previous work samples of SRM 950a, ignited in the tube furnace for one hour at 900 °C, had a weight loss that agreed to within 0.005 percent of samples from the same bottle of 950a ignited in an open crucible for one hour at 900 °C. Samples of high-purity, 99.98 percent, uranium metal were ignited at 900 °C for one hour after slow oxidation at a lower temperature. The increase in weight, taking into consideration the metallic impurities, was from 0.07 to 0.12 percent more than the calculated weight increase to produce U_3O_8. This meant that the same stoichiometry was not obtained for these two starting materials and further investigation was necessary. Ignitions at temperatures from 900 to 1050 °C were tried on SRM 950a and the metal. It was found that the higher temperature (Table 1) gave greater ignition losses on 950a, all less than stoichiometric, and increased length of ignition times also gave larger ignition losses (Table 1). Experiments with ignition in an oxygen atmosphere (>99%) showed slowly increasing losses with increasing temperatures to 1000 °C (Table 2). Ignition in oxygen after ignition in air at 1050 °C appeared to give reproducible ignition losses. Further investigation showed that several hours, usually overnight, ignition at 1050 °C in air and then

Table 1. Weight loss on ignition of 1 gram samples of SRM 950a.

		Loss in weight	
Temperature (°C)	Ignition time[a]	Sample 1 (%)	Sample 2 (%)
900	1	0.096	0.098
"	17	0.108	0.111
"	18	0.109	0.107
"	34	0.112	0.115
1000	1	0.127	0.129
"	2	0.132	0.136

---

[a] Total ignition time in hours at each temperature.

Table 2. Weight loss on ignition of 1 gram samples of SRM 950a in an oxygen atmosphere.

Temperature[a] (°C)	Loss in weight Sample 1 (%)	 Sample 2 (%)
450	0.050	0.049
550	0.061	0.058
650	0.073	0.070
750	0.077	0.074
800	0.079	0.076
850	0.082	0.080
900	0.085	0.082
950	0.087	0.085
1000	0.088	0.087

---

[a] Ignited for one hour at each temperature.

an ignition in oxygen from 700 °C to 1000 °C gave an oxide that was reproducible. Repeated ignition cycles in air and then in oxygen showed nearly constant weight (Table 3). Since calculation showed both SRM 950a and the metal to have the same stoichiometry after ignition in air at 1050 °C for 16 hours followed by one hour in oxygen at 850 °C, several uranium samples with different histories were ignited by this procedure and titrated coulometrically by George Marinenko of the Microchemical Analysis Section [1,2,3,4]. The results are given in Table 4. The five samples represent starting materials of metal; nitrate, roasted at 850 °C; and a peroxide precipitate roasted at 800 °C. The first four samples have less than 100 ppm impurities and the fifth sample, the metal, has been corrected for an assay of 99.977 percent which had been determined by the same coulometric titration. Impurities detected in the metal are about 200 ppm which agrees very well

Table 3. Weight loss on repeated ignition of 0.5 gram samples of SRM 950a.

Temperature (°C)	Ignition time (hours)	Atmosphere	Loss in weight Sample 1 (%)	Loss in weight Sample 2 (%)
900	1	air	0.075	0.075
1050	16	"	0.101	0.110
850	1	O_2	0.079	0.079
"	"	"	0.080	0.080
1050	16	air	0.102	0.114
850	1	O_2	0.082	0.082
"	"	"	0.082	0.081
1050	16	air	0.105	0.117
850	1	O_2	0.085	0.085
"	"	"	0.084	0.084
1050	16	air	0.105	0.115
850	1	O_2	0.086	0.085
"	"	"	0.086	0.085
"	16	"	0.086	0.085

with the assay. When this correction is made, the assay value of the oxide, 99.929 percent, is in good agreement with the other four samples. These results indicate that the ignition procedure will give samples of the same stoichiometry regardless of the starting materials.

This ignition procedure was used for all samples in this paper.

Table 4. Coulometric assay of ignited U_3O_8 samples.

Sample	Sample No.	Assay (% U_3O_8)	
SRM 950a	1a	99.904	
	1b	99.946	
	2	99.918	
	Average =	99.923	s.d. = 0.023
SRM U-0002	1a	99.917	
	1b	99.911	
	2	99.960	
	Average =	99.929	s.d. = 0.027
"U238"	1a	99.913	
	1b	99.932	
	2	99.919	
	Average =	99.921	s.d. = 0.010
"U235"	1a	99.928	
	1b	99.918	
	2	99.921	
	Average =	99.922	s.d. = 0.005
Dingot	1a	99.929	
	1b	99.923	
	2	99.934	
	Average =	99.929	s.d. = 0.005

C. U_3O_8 Stoichiometry

The stoichiometry of U_3O_8 was investigated further in hopes of finding an easily reproducible ignition procedure that would give stoichiometric U_3O_8. Some of the previous work indicated the rate of cooling could affect the ignition loss and there have been personal communications indicating slight changes in ignition loss at different geographic locations having different altitudes or atmospheric pressures. A series of thermogravimetric analysis (TGA) ignitions were conducted varying the air pressure and oxygen content. Accurate cooling experiments could not be carried out conveniently with the equipment available. Figure 1 gives blanks at two pressures of air showing that the instrument was not sensitive to different pressures as long as they were constant. The temperature was determined by using a calibrated platinum-platinum rhodium thermocouple to correct the chromel-alumel thermocouple used on the equipment. The correct temperatures are marked on the figures. Figure 1 also gives TGA curves on 100 mg samples of SRM 950a at decreasing atmospheric pressures. To obtain the greatest sensitivity, 100 mg was suppressed by the instrument and the sensitivity was increased to the maximum of 100 μg per division. It can be seen from the curves that the loss in weight occuring near 900 °C shifts to lower temperatures with decreasing pressures. Figure 2 shows a similar shift when the oxygen content is reduced. The first curve in Figure 3 is a cooling curve after ignition of SRM 950a to 1000 °C in air and indicates some gain in weight below 850 °C. The same sample being reignited is shown in the second curve and shows approximately the same loss at 900 °C as a sample being ignited for the first time. The third curve is the same sample reignited after it had been cooled by quickly removing it from the furnace. The instability of the TGA instrument does not allow a determination of whether all the weight gain occurs during the cooling or if part of the gain is during the heating period of the next ignition.

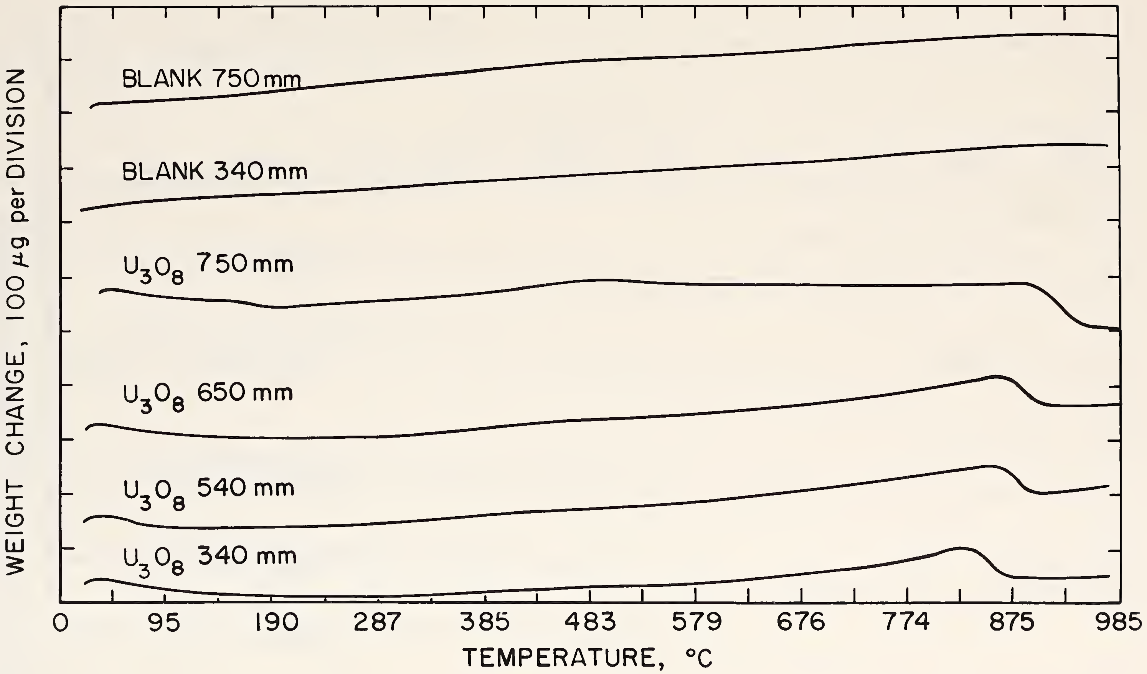

Figure 1. Thermogravimetric analysis curves of blanks and 100 mg U_3O_8 samples under various pressures.

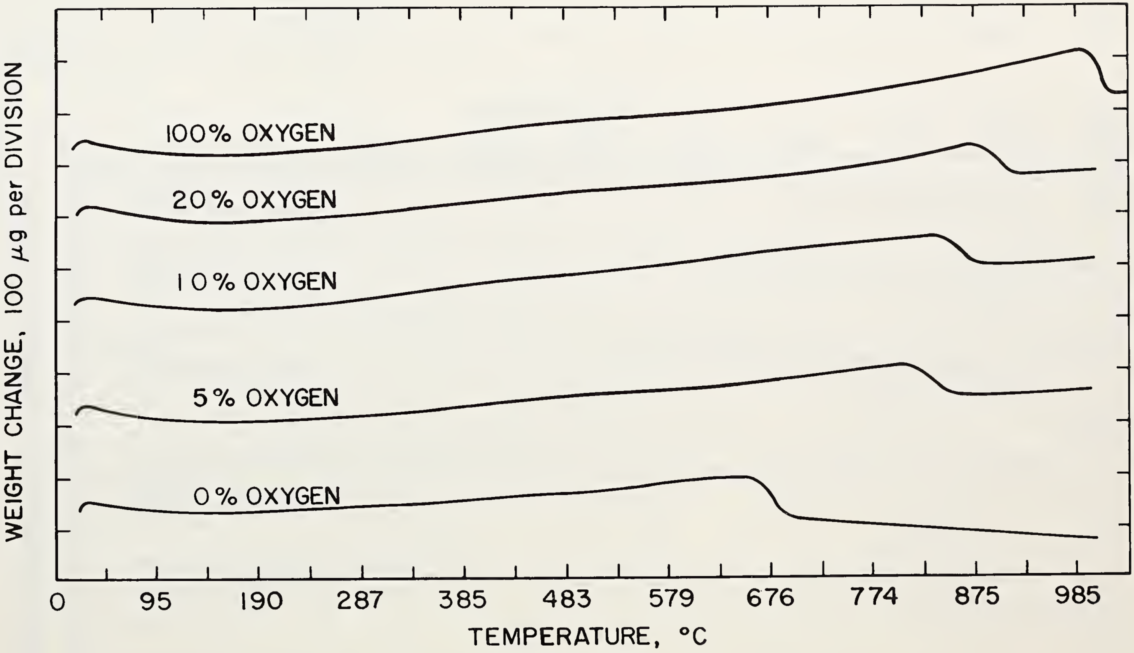

Figure 2. Thermogravimetric analysis curves of 100 mg U_3O_8 samples in various percentages of oxygen.

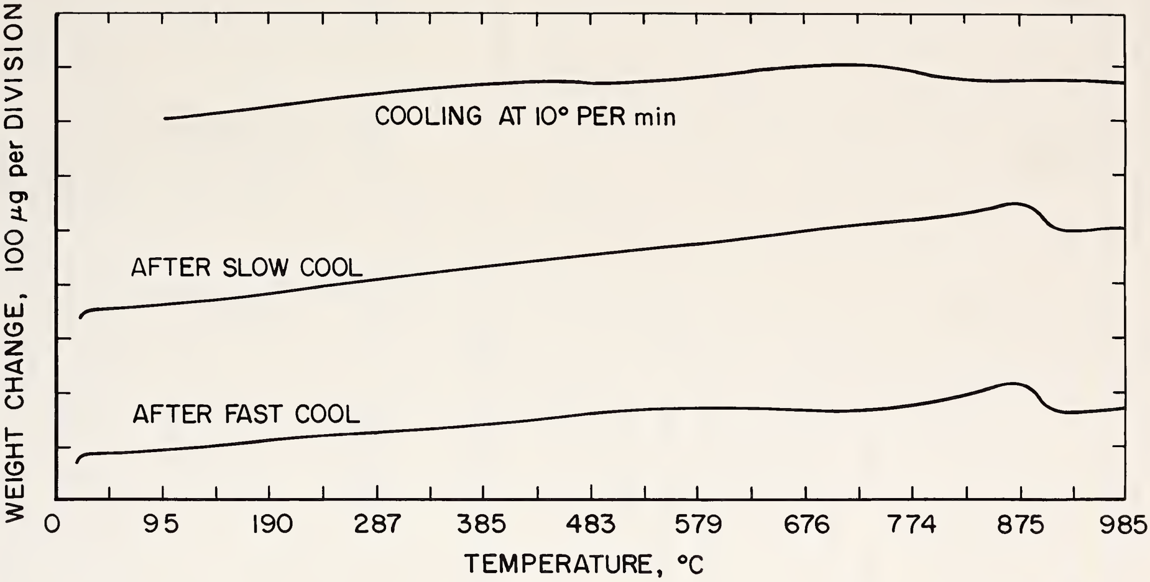

Figure 3. Thermogravimetric analysis curves of 100 mg U_3O_8 samples with different cooling rates.

One gram samples of SRM 950a were ignited in a tube furnace to obtain ignition losses under different cooling procedures as well as under various temperatures and pressures. These ignitions were carried out using the same equipment and under the same conditions, except as noted, that were used for all samples in the isotopic program as described later in Section 6,B,3. Three rates of cooling were used in addition to the one normally used. For convenience the rates of cooling are identified as follows: "fast", meaning that the boat containing the sample was quickly pulled into an iced portion of the quartz tube; "normal", meaning that the furnace was quickly moved back from the sample area of the tube; "slow", meaning that the furnace was slowly moved back from the sample area of the tube over a period of approximately 15 minutes; "very slow", meaning that the furnace was turned off and allowed to cool over a period of several hours while still covering the sample area. Table 5 shows the average loss on ignition of at least two samples ignited for one hour at the temperature indicated.

Table 5. Ignition loss on 1 gram samples of SRM 950a under different cooling rates

	Cooling rate			
Temperature (°C)	Very slow (% loss)	Slow (% loss)	Normal (% loss)	Fast (% loss)
850			0.076	
900		0.084	0.087	0.096
950		0.086	0.102	
1000	0.085	0.090	0.114	0.120
1050	0.082	0.094	0.126	

The results show not only a significant increase in loss on ignition at increasing temperatures but increasing loss with faster cooling rates. The results indicate that a very slow cooling rate might give a reproducible ignition loss but that it would be nonstoichiometric to approximately the same extent as the ignition described in Section 6,B,3. The TGA curves, the assay, and the ignition data indicate that the U_3O_8 is very close to stoichiometric after the loss at approximately 925 °C in air is complete as shown on the TGA curves but that weight is picked up, apparently oxygen by the U_3O_8, in amounts that vary depending on the cooling rate, temperature of the ignition and length of ignition.

In an air atmosphere at a reduced pressure of 550 mm of Hg the loss on ignition for one hour at 900 °C was 0.104 percent compared to 0.087 percent at a pressure of 750 mm with a normal cooling rate for both. When a slow cooling rate was used the losses were 0.083 percent at the reduced pressure and 0.084 percent at atmospheric pressure. These results indicate that samples ignited at higher elevations could have an assay as much as 0.02 percent higher than the same sample ignited at sea level if normal cooling rates are used.

Ignitions in 5 and 10 percent oxygen atmospheres resulted in greater losses. The loss on two samples at 1050 °C for one hour in 10 percent oxygen with normal cooling was 0.166 and 0.172 percent. The loss at 1000 °C for one hour in 5 percent oxygen with normal cooling was 0.175 and 0.187 percent, with slow cooling was 0.154 and 0.141 percent, and with very slow cooling after one hour at 1050 °C was 0.091 and 0.093 percent. An ignition loss of approximately 0.15 percent would be required on this sample to obtain stoichiometric U_3O_8. These ignitions in 5 and 10 percent oxygen with normal cooling exceed the 0.15 percent loss but again with slower cooling the loss decreases until it approaches, within 0.01 percent, the loss found in an air ignition with a very slow cooling. It might be possible to obtain stoichiometric U_3O_8 by an ignition in an atmosphere of less than 20 percent oxygen to an exact ignition temperature and by a very carefully controlled cooling rate but, it would not be practical because of the difficulty in reproducing these ignition conditions. For this reason the procedure developed in the previous section (2,B) was used for all ignitions in the SRM characterization.

D. Aliquoting of Uranium Solutions

The preparation of "U235" and "U238" separated isotope calibration mixes for the range of 10 percent ^{235}U to 90 percent ^{235}U could be done by blending weighed portions of the separated isotopes; but, outside this range and for all the "U233" additions for isotope dilution determinations of the minor isotopes, aliquoting of solutions would be required. The aliquoting needed to be accurate to within a few parts in ten thousand, and preferably to one part in ten thousand, so that the aliquoting uncertainty would not contribute significantly to the overall uncertainty in these determinations.

An automatic buret was investigated to determine if it could be used for aliquoting. Repeated aliquots of 5 ml were found to differ by as much as 0.01 ml, which was twenty parts in ten thousand and would not be satisfactory. Since in this laboratory it has been found difficult to do volume aliquoting to an accuracy of much better than one part per thousand, it was decided to try weight aliquoting.

A teflon bottle used as a "squirt" bottle was investigated for use in aliquoting by weight. The regular cap on the teflon bottle was replaced with a similar cap that had inserted in it a piece of polyethylene tubing shaped for use as a "squirt" bottle and the outside end of the tubing was covered with a polyethylene cap to prevent evaporation. When the weight of aliquot obtained by weighing the "squirt" bottle before and after delivery of the aliquot, was compared with the weight of solution delivered to a glass weighing bottle, the discrepancy was 0.5 to 1 mg less in the glass weighing bottle. Since the weighing bottle with solution lost about 0.5 mg per minute when covered with a filter paper having a small hole, as had been used for the aliquot checking, and since the aliquoting required about one minute, the weight of aliquot using a "squirt" bottle should be accurate to within 1.0 mg. It was decided to use aliquots of at least 3 g of solution from the "squirt" type teflon bottle which should give aliquots accurate to at least three parts in ten thousand. This procedure was used on the "U233" isotope dilution of SRMs U-005 through U-930.

A better weight aliquoting technique using plastic syringes was developed before the remaining aliquoting was done. In this technique the weight of solution was determined and the cap of the teflon bottle was quickly replaced with a rubber serum septum. A platinum needle was inserted thru the septum and a short second needle served as a vent. A 2.5, 5 or 10 ml plastic syringe, with the rubber plunger covered by a thin teflon sheet to prevent possible contamination, was attached to the Kel-F hub of the platinum needle and the desired amount of solution was drawn into the syringe. After a small amount of air was drawn into the tip of the syringe, the syringe was disconnected and quickly capped with a Kel-F cap. The syringe was wiped with a damp paper towel to remove any static charge and weighed. The aliquot was delivered from the syringe and the syringe was capped, wiped and reweighed. Repeated weighings of the filled or empty syringe gave weights that duplicated to within 0.1 mg. Aliquoting by this procedure [5,6] has been shown to be accurate as well as precise to at least one part in ten thousand.

E. Preparation of SRM Samples by Union Carbide Nuclear Company

The 18 SRM samples were supplied through the AEC from Union Carbide Nuclear Company, Oak Ridge, Tennessee.

All but SRM U-0002 were prepared at Oak Ridge by the following procedure.

Approximately 1900 grams of uranium hexafluoride of the specified isotopic concentration was withdrawn from the cascade. The hexafluoride was liquified, thoroughly mixed, vacuum transferred to a large nickel cylinder, cooled with liquid nitrogen, "knocked out" into a 15 liter always-safe polyethylene container, and hydrolyzed with 8 liters of cold distilled water. After mixing, the solution was evaporated to dryness in platinum dishes under infrared lamps and the uranyl fluoride was converted to urano-uranic oxide by pyrohydrolysis at 800 °C. This oxide was dissolved in 2 N nitric acid and the solution was filtered into a clean always-safe container and thoroughly mixed by inverting and rolling the container.

Portions of the solution containing 100 to 125 grams of uranium were transferred to Vycor beakers and the uranium was precipitated by adjusting the pH to 1.0 with ammonium hydroxide, adding 1.3 ml of 30 percent hydrogen peroxide per gram of uranium, and allowing the $UO_4 \cdot 2H_2O$ to settle at least 16 hours. The supernatant liquid was decanted, the precipitate was washed, and after allowing the precipitate to settle, the supernatant was again decanted. The precipitate was filtered, washed, transferred to a platinum dish, and ignited to urano-uranic oxide at 850 °C for 16 hours. This oxide was ground in a boron carbide mortar, sieved through a 60 mesh screen, and blended. All of the oxide was then placed in a polyethylene bottle and again blended for 10 minutes.

The U-0002 sample was purified by a cupferron precipitation and an additional peroxide precipitation in addition to the procedure used on the other 17 SRMs.

These samples were checked by spectrographic analysis for 64 possible impurities. The total impurities detected on each of these samples were less than 50 ppm. A typical spectrographic analysis is given in Table 6. If all the other elements not detected were present at their limits of detection the total could be approximately 200 ppm, this, however is highly improbable.

For each SRM sample, except the U-0002, one kilogram of uranium in the form of oxide was shipped to the National Bureau of Standards. Twenty kilograms of SRM U-0002 were shipped.

Table 6. Spectrographic analysis of SRM U-050.

Element	Limit of detection (ppm)	Detected[a] (ppm)	Element	Limit of detection (ppm)	Detected[a] (ppm)
Ag	0.3	-	Pt	1	1
Al	1	-	Rb	10	-
As	3	-	Re	5	-
Au	1	-	Rh	1	-
B	0.1	1.5	Ru	1	-
Ba	10	-	Sb	1	-
Be	1	-	Sc	1	-
Bi	1	-	Si	1	3
Ca	1	-	Sn	1	-
Cd	1	-	Sr	1	-
Co	1	-	Ta	1	-
Cr	1	-	Th	1	-
Cs	10	-	Ti	0.3	-
Cu	0.1	0.5	Tl	2	-
Fe	1	2	V	1	-
Ga	1	-	W	1	-
Ge	1	-	Zn	20	-
Hf	1	-	Zr	1	-
Hg	1	-	Lanthanide Elements		
In	3	-			
Ir	1	-	La	1	-
K	5	5	Ce	1	-
Li	1	-	Pr	1	-
Mg	0.1	-	Nd	1	-
Mn	1	-	Sm	1	-
Mo	1	-	Eu	1	-
Na	1	2	Gd	1	-
Nb	1	-	Tb	1	-
Ni	1	5	Dy	1	-
Os	20	-	Ho	1	-
P	3	-	Er	1	-
Pb	3	-	Yb	1	-
Pd	1	-	Lu	1	-

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[a] The symbol "-" means that the element was looked for but not found.

These samples were packaged at NBS for distribution to AEC approved facilities. One gram of uranium in the form of oxide, weighed to within 5 mg, was transferred to glass micro bottles. A thorough cleaning of the hood was conducted between SRM samples to prevent isotopic contamination by a previously weighed sample.

F. Preparation of Separated Isotope Samples by Union Carbide Nuclear Company

The "U233" (Lot No. 3), "U235" and "U238" separated isotope samples were supplied by the AEC through Union Carbide Nuclear Company. The original "U235" sample, pile waste, was enriched by Calutron treatment. The sample was then purified by two ether extractions, a hydrogen peroxide precipitation and volatilization of the vanadium as vanadyl chloride. The "U238" sample was prepared from natural uranium in a similar manner. Spectrographic analysis indicated approximately 50 ppm detectable impurities in these samples.

G. Solution Preparation for Mass Spectrometric Analysis

Solutions were prepared with a uniform matrix so they would give a uniform response on the mass spectrometer (Section 4,G and 4,H). All solutions were prepared to contain 5 mg U/ml in nitric acid (1+19). Impurities, especially alkali metals, were kept to a minimum. The reagents used were selected for their high overall chemical purity as well as being checked for any uranium contamination. The uranium isotopic SRM samples and the separated isotope samples were of high chemical purity and did not require further purification.

Although the solutions described in this publication did not require further chemical purification, a chemical purification step is included when the isotopic composition is being determined on an unknown sample so the unknown and standard are as near the same purity and concentration as possible. The purification step used is an anion exchange separation. For samples containing up to a few milligrams of uranium, a column (0.6×7 cm) of strongly basic anion resin which has been cleaned by alternately adding 0.3 N nitric acid and nitric acid (1+1) is used. The sample is dissolved in a minimum of nitric acid (1+1) and added to the column. Most elements are not held by the resin in nitrate form [7] and are quickly eluted with nitric acid (1+1), a maximum of 3-4 ml of nitric acid (1+1) is used for both the sample and the elution of the impurities. The uranium is then eluted with 0.3 N nitric acid. The uranium eluate is evaporated to dryness and then dissolved in sufficient nitric acid (1+19) to give a solution containing 5 mg U/ml of solution. On samples containing low concentrations of uranium, this anion exchange separation should be repeated. Two anion exchange separations have proven adequate for uranium at the ppm level in glass samples [8]. Other separation techniques may be required for some samples, but the solutions prepared for mass spectrometric analysis should be as nearly as possible identical to the calibration solution.

3. MASS SPECTROMETRY - INSTRUMENTATION

A. Introduction

The objective of this section is to briefly discuss some of the unique instrumental features and to indicate their effect in the measurement method. Instrumental parameters restrict the selection of conditions for certain analytical procedures and are frequently the limiting or decisive factor in selecting optimum conditions to determine isotopic composition. All probable sources of systematic error attributable to the mass spectrometers must be identified, eliminated, reduced or controlled before bias components associated with the ionization process can be studied effectively. Thus, the mass spectrometer is the second area to be mastered before the maximum amount of information can be extracted from each analysis. Whenever applicable, some historic information is included because of the long and continuous nature of the instrumentation development period.

B. General Description of Mass Spectrometer

The mass spectrometers were single focussing, solid sample instruments with a 12-inch radius of curvature 68° analyzer tube and 60° sector magnet. During the past decade there were no newly discovered basic or fundamental innovations in the spectrometers utilized for uranium analysis, but all of the major component systems were repackaged, rearranged and, in many instances, extensively modified (see Appendix I). The basic 12-inch 68° analyzer tube mass spectrometer and some of the developmental changes are described in other publications [9,10,11].

C. Source

The source is a linear thin lens with each succeeding lens being approximately twice as far from the ionizing filament as the previous lens [9]. The source was constructed without baffles or skirts to facilitate the maximum pumping speed possible in the vicinity of the filaments. Initially, the source defining slit was movable and was adjusted by an external micrometer screw mounted in the source housing. The major shortcoming of this type assembly was the inability to precisely determine or reproduce a given slit width once the micrometer was moved or the source was disassembled for cleaning or maintenance purposes. The results of this unavoidable variation in the slit width was a change in transmission. Since sample filament temperatures cannot be measured directly, the analytical procedure is based on maintaining a constant signal intensity within a limited temperature range with all other focal parameters constant. Thus, the effect of slit variations was a sample filament temperature compensation to maintain the intensity as a fixed parameter. If this temperature compensation was large enough and remained undetected, it would be the cause of apparent differences in isotopic composition between different sources, shifts in data between source cleanings, or sudden shifts in data on a source when the micrometer screw was inadvertently repositioned.

The problem was solved by redesigning the source [10] so that the micrometer adjustment was replaced by a slit assembly formed by two movable knife edges firmly fixed in position by screws. The slit adjustment is external to the source housing and is made on the work bench where the width can be accurately determined with gauges. The newly designed source can be disassembled and cleaned without a compulsory change in the slit width or, if necessary, the slit knife edges are removable for cleaning purposes and the desired slit width reproduced accurately.

The redesigned source also included the addition of a "Z" focussing lens which increased the transmission of the 12-inch spectrometer by a factor of approximately 3. The increase in transmission permitted the option of obtaining the standard signal intensity at slightly lower filament temperatures and with a correspondingly lower rate of fractionation. Since signal intensities between 5×10^{-10}A and 1×10^{-9}A are obtainable without large changes in the isotopic composition with time, the lower isotopic abundance limit at which satisfactory measurements could be made without using ion multiplier detection was extended to the 100 ppm level with a 95 percent confidence limit of approximately 1 percent.

D. Collector

The NBS collector is a conventional Faraday cage collector and has a transmission grid and a series of suppression grids [9]. Although the transmission grid monitors a fraction of the total ion current (50% or less), the prime function is to mask the suppression grid system from the ion beam. The grid is made of 0.030 inch tungsten ribbon separated by an opening of equal width. The width of the tungsten ribbon is large enough to completely shield the suppression grids from the ion current. The purpose of the suppression grid system is to provide cubic suppression of secondary particles between the defining slit of the collector and the transmission grid. By applying appropriate potentials to the grids, a nearly constant grid response is obtained as ion currents of the isotopes are switched on and off the Faraday cage. A collector that is dirty or exposed to large quantities of the alkali elements will produce an excessive number of secondary electrons. Thus, an adequately designed collector, "aged" with time, will gradually acquire a thin film deposit of extraneous material on various surfaces. As the level of contaminant increases the number of scattered particles increases and some of these particles are collected on the transmission grid. When this stage is reached, the grid response changes from a constant for ion currents switched on and off the Faraday cage to a variable that increases with time. The change in the constant nature of the grid response is the prime indicator in determining the need for a collector cleaning. The suppression grids extend the operational life of a collector beyond the normal expectancy for a non-grid system, and eliminate a random bias component which can be several tenths of a percent. This bias component is dependent upon the energy of the ions, magnitude of the ion current, and the degree of cleanliness of the collector.

E. Ion Multipliers

The ion multipliers were either 8 or 12 stage units constructed of copper-beryllium dynodes. Although these units were capable of operation at high gain, the standard procedure was to operate at abnormally low gains of 30-100 for uranium isotopic measurements. Thus, the analytical objective of the multiplier was to provide sufficient gain to maintain a minimum amplified output signal from the vibrating reed electrometer (VRE) of approximately 10 mV (100 chart divisions) for operation of the expanded scale recorder in measuring minor isotope ion currents. Additional objectives were (1) to obtain nearly uniform gain (flat top peaks) as the ion beams moved across the first dynode, (2) to obtain long term stability and (3) to operate at approximately the same background noise level as the standard collector.

Ion multipliers were used sparingly in analyzing uranium SRMs and were installed as detector only when the precision of ^{234}U and ^{236}U measurements was deemed to be unsatisfactory with conventional collectors. Prior to the development of the "Z" lens source, the general guideline was to use ion multiplier detection when the abundance of a uranium isotope was equal to or less than 0.1 atom percent. At a 0.1 atom percent composition it was possible to use both types of detectors and obtain direct evaluation of the accuracy of the total bias correction (filament and ion multiplier) for multiplier measurements. The standard procedure was to determine experimentally a single correction factor which includes a component for the ion multiplier and to use this single correction factor to correct for all bias effects.

F. Measuring Circuit

The measuring curcuit consisted of (1) two vibrating reed electrometers (VRE) operated as a master-slave combination and (2) an expanded scale recorder.

1. Slave VRE

The slave unit was used to monitor that portion of the total ion current intercepted or collected by the transmission grid. The input resistor for the slave VRE was always 10^{10} ohm and the output of the unit was displayed by the X_1 pen of a dual pen strip chart recorder. The grid signal provided a quick and reliable means of establishing uniform quality control for all analyses and facilitated the detection of collector failures and/or abnormal collector response. Abnormal or sudden changes in grid response were indicative of malfunctions such as loss of suppression potential, unstable suppression potentials and broken or malaligned grid wires.

The stability and behavior (growth or decay) of the grid signal are used as STOP or GO flags to reject or accept an analysis without ever measuring the ion currents of the isotopes on the Faraday cage. Concentrations of the alkali elements, either from the filament assembly or the uranium sample, produce sharp erratic spiking of the grid signal, even when these isotopes were not focussed on the grid or Faraday cage. This particular response was a clue to their presence which was quickly verified by scanning to the appropriate mass positions. Even though the concentration of these elements was not known, any concentration that produced the random spiking response was considered to be undesirable. If this response occurred within an analysis and did not end before the ratio measurement was started, the analysis was terminated and no data were taken. If this response was reproducible for different filament loadings, the contaminant had to be identified and the necessary measures were taken to reduce the background below the critical level.

2. Master VRE

The master VRE is used to measure the ion current collected on the Faraday cage. Input resistors of 10^{11} and 10^{10} ohms were available on all units and were switched in or out of the measuring circuit at the option of the analyst. Although 10^{9} ohm resistors were available on some units, they were not normally necessary for uranium analysis. Input resistors of 10^{12} ohms were not used because they were found to be non-linear.

3. Expanded Scale-recorder

The 10 mV and 100 mV outputs of the master VRE are utilized in the expanded scale recorder circuit which is discussed in detail in another report [9]. These two outputs permitted the design and operation of the unit so that either standard (unexpanded) or expanded modes of operation were selectable at the option of the analyst. In the standard mode of operation, a 10 mV output of the master VRE produced full scale deflection of 100 recorder chart divisions. When operated in the expanded mode, a 100 mV output from the VRE produced 10 full chart widths of deflection (1000 recorder chart divisions), and by selecting the proper potential for the bottom of the slide wire, the recorder is balanced "on scale". Independent of the mode of operation, there is a recorder error component due to dead zone and linearity of the slidewire which is approximately 1/4 of a chart division (0.25% of full scale deflection). There is also an error component in peak height determinations of about 1/4 chart division. The total error of approximately 1/2 chart division from these two sources is always present, is constant in magnitude and is independent of peak height. This error contribution, as a percentage of the peak height, is a variable that reduces to approximately 0.5 percent for a maximum deflection of 100 chart divisions for the standard recorder, or to 0.05 percent for a peak height approaching 1000 chart divisions for the expanded scale recorder. Thus, the limit of error of bias for the standard mode of operation is 0.5 percent, and drops to 0.05 percent for the expanded mode of operation because the uncertainty due to recorder and peak height determination is a smaller percentage of the larger deflection. The net result is a factor of 10 reduction in the systematic error contribution from the recorder when operated in the expanded mode. A secondary benefit of expanded operation is more uniform wear of the slidewire over its entire length and, consequently, a more linear response, than when operated in the standard mode which produces excessive wear at one end of the slidewire.

Since the benefits of an expanded scale recorder are not inherently obtained by moving the functional switch to the expanded position, the analyst must, when possible, avoid operating the measuring circuit with less than 100 chart divisions of deflection. The limit of error for this operational condition is 0.5 percent and is independent of the mode of operation. To obtain maximum precision, the measuring circuit must be operated so that recorder deflection is a maximum for the ion current collected on the Faraday cage. Unless it was impossible or impractical to achieve the necessary ion current intensity, the expanded scale circuit was always operated so that the minimum deflection was 200 chart divisions. Because of the recorder dead zone, slidewire non-linearity and the inability to determine the true resistance of the VRE decade resistors, the minimum error statement of a direct isotopic ratio determination was 0.00002.

4. MASS SPECTROMETRY - MASS DISCRIMINATION EFFECTS AND AN EVALUATION OF PARAMETERS

A. Introduction

Good analytical procedures are based upon (1) a knowledge of the sources of bias, (2) establishing control of the various parameters that contributed to this bias and (3) selecting an optimum combination of parameters that is uniform and reproducible for each analysis. Even when the error contributions from chemistry and the instrument are negligible, large bias components are possible because of irregularities in the sample mounting or the pattern of heating the filaments to obtain ion emission. The difference between the observed and true isotopic ratio is not necessarily small [6,13,14,15] and no effort is expended to obtain a minimum deviation from the true value or to accurately ascertain the magnitude of each component of the bias. The effort is to determine the degree of constancy of the isotopic ratio under various conditions, choose the best set of conditions, and verify the constancy of the total bias under identical experimental conditions for chemically prepared calibration mixes of known isotopic composition and the samples to be calibrated. Thus, a single, experimentally determined correction factor is calculated and used to correct for all bias effects for all ratios.

B. Mass Discrimination Effects

For thermally produced ions the light isotope is preferrentially evaporated and ionized with respect to the heavier isotopes of an element. This effect is temperature dependent and is a function of the mass. The preferrential depletion of the light isotope was observed for uranium and all other absolute isotopic abundance studies by the Analytical Mass Spectrometry Section [5,6,13,14,15,16,17,18,19]. The bias due to preferrential depletion of isotopes is referred to in this report as filament bias.

For uranium this effect was studied by measuring the $^{235}U/^{238}U$ ratio for many variations and permutations of the analytical parameters and over a wide range of isotopic ratios. The dependency of the bias on temperature, its irreversible nature, and its consistency under controlled analytical conditions, over the range of ratios represented by SRMs U-050 through U-930, formed the basis for the conclusion that the observed bias was due to the effects of ionization and evaporation in the source and was independent of isotopic composition. By selecting different combinations of parameters, usually temperature, time and sample size, the filament bias for uranium $^{235}U/^{238}U$ measurements can be made additive, zero or subtractive. For low temperature analysis of a 200 µg uranium sample the filament bias of the observed $^{235}U/^{238}U$ ratio is approximately 0.5 percent. A high-temperature analysis of the same amount of material gives a $^{235}U/^{238}U$ bias of approximately 0.2 percent. The only difference in parameters for these techniques is a significant increase in sample filament temperature for the high temperature procedure. Further increases in sample filament temperature can make the filament bias zero or even subtractive. Thus, one should be aware that preferential depletion occurs during thermal ionization even if the observed bias is small or nearly constant for long periods of time or when the measured ion current ratio is identical to its composition in the sample.

By developing fixed analytical procedures in which all parameters are constant or maintained within narrow limits, it was demonstrated that bias effects due to fractionation are a characteristic of the combination of analytical parameters used for the measurement and are reproducible to better than 0.05 percent for a given procedure. The degree of accuracy achieved in evaluating bias effects due to fractionation is directly dependent upon the ability to control and reproduce all parameters between sample loadings. Consequently, it was necessary to investigate some of the parameters that controlled the rate of depletion of the sample reservoir and to develop the means of starting each analysis with the same amount of material on the sample filaments. Even after the chemistry fulfilled one of its functions and supplied solutions of uniform concentration, it was necessary to look for conditions during sample mounting and the mass spectrometric analysis that could produce an apparent loss in sample size by either a failure to convert to the proper oxide or by material simply flaking off the filament surface.

C. Filament Temperature

Filament temperature is one of the more critical parameters to be controlled because evaporation and the rate of depletion of uranium from the filament are primarily a function of temperature. Ideally, it is desirable to measure the temperature of each filament and maintain it within the same limits for each analysis. The methods used to control sample filament temperatures were constant current control and a combination of filament current and signal intensity. The ionizing filament temperature was determined by adjusting to a constant rhenium signal intensity and by direct measurement with an optical pyrometer.

1. Sample Filaments

Strict reliance on a constant filament current to produce a constant temperature for a large lot of rhenium ribbons was unacceptable for precise isotopic measurements. Dimensional variations within a lot of rhenium ribbon, 0.001×0.030 inch, were large enough to cause a 1 A difference for filaments at 2160 °C. Sample filaments were normally operated at less than 1650 °C and the current variation attributed to dimensional variations was at least 0.3 A. Dimensional variations in the thickness of ribbon between lots supplied by commercial manufacturers were found to be large enough to cause a definite shift in filament currents at a constant temperature.

Although the preferred method of sample filament temperature control was indirect and imperfect, it accomplished the goal of limiting the sample filaments to a constant temperature range for each analytical procedure used. It was based on the assumption, that, if all parameters were maintained nearly constant and approximately the same amount of uranium was loaded on the filaments for each analysis, the signal intensity was a coarse measure of the filament temperature. Therefore, the signal intensity for each analytical procedure was restricted to very narrow limits and was reproduced for each analysis of a given procedure. Using the long term performance of many sample loadings, ion current intensity - filament current relationships were established. This type of relationship was used as a common reference for each uranium procedure. Failure to maintain the signal intensity within the prescribed limits for a fixed current range was sufficient reason to terminate an analysis without any further consideration. This type of control was in some respects tenuous because it was subject to distortion by failure to properly focus for maximum intensity, malfunction in the focus control circuit, changes in the ionization efficiency of the filaments or the transmission efficiency of the source. In spite of these handicaps, the reproducible signal intensity method has worked very well for uranium and many other elements, in lieu of a direct method of measuring sample filament temperatures.

By measuring the ionizing filament temperature over the same current range as the sample filaments were operated, estimates of the sample filament temperature limits were made for analysis of 200 μg samples. The minimum sample filament temperature for an analysis was 1200 °C (∿2.2 A) and the maximum temperature used for any of the analytical procedures was approximately 1600 °C (∿3.0 A). Analysis of SRM U-500 at random temperatures over the entire range with all other parameters maintained as constants gave a scatter in the observed $^{235}U/^{238}U$ data of 0.3 to 0.5 percent. By operating at either extreme or even in the middle of this temperature range the scatter in observed $^{235}U/^{238}U$ ratios was reduced by a factor of three. It was concluded that sample filament temperature limits of less than 200 °C were essential for ratio measurements with a 95% confidence level (C.L.) of better than 0.1 percent.

2. Ionizing Filaments

The optimum temperature of the ionizing filament was selected to provide efficient ionization, long filament life, and to deplete the interstitial oxygen which was a source for formation of the UO^+. The Re^+ signal from the hot ionizing filament was useable as a reference point to precisely reproduce the optimum filament temperature for each analysis. This technique was based on the assumption that a nearly constant temperature would yield approximately the same Re^+ signal intensity for all filaments. Verification of this assumption was initially made by installing a clear plastic source flange and using an optical pyrometer to determine filament temperatures. Rhenium filaments at 2150 °C yielded a ^{187}Re ion current of approximately $6{\times}10^{-12}A$. This method was believed to be reproducible to within ±20 °C for most rhenium filaments.

Modification of the source flange to include a small diameter window made temperature determinations with an optical pyrometer the preferred method. Because the scale of the pyrometer was calibrated in increments of 20 °C, the optimum temperature was changed to 2160 °C for convenience. Pyrometer measurements quickly revealed that the temperature drifted downward approximately 20 °C during the first few minutes of heating. After readjustment to 2160 °C, the temperature remained nearly constant for long periods of time. As the filament developed cracks or "hot spots" the temperature increased, and continued to increase until burnout occurred. The response of the rhenium signal closely paralleled the trends of the temperature, and as the filament developed "hot spots" the signal intensity started a continuous growth cycle that ended in filament burnout.

There are shortcomings in the exclusive use of either of these methods but the optical pyrometer is superior and more precise. The constant rhenium signal intensity method is dependent upon any parameters which change the transmission of the source or the ionization efficiency of the filament. Pyrometer measurements are free of these restraints and only require a stain free window and a minimum of shadow on the filament. Monitoring the rhenium signal was not discontinued but was used as a secondary reference to mutually support the pyrometer measurements or serve as an indicator of abnormal instrumental or analytical conditions.

D. Sample Size

The optimum amount of uranium necessary for an analysis of the SRMs was determined experimentally and is primarily a product of performance and analytical experience. The prime requisite was the ability to complete an analysis using only a small fraction of the total sample on the filament and to avoid making ratio measurements under the gross fractionation conditions of complete sample depletion. A large uranium sample size also made it possible to measure a wide range of ion current ratios under the same thermal fractionation conditions. Some of the prime indicators used to make a decision about the optimum sample size were the rate of change of the $^{235}U/^{238}U$ ratio, the maximum signal intensity obtainable and the length of time it was maintained.

Initially, approximately 400 µg of uranium was considered to be optimum for an analysis and was used for several years. Prior to use of a "Z" lens source the sample size was reduced to approximately 200 µg because of improvements in the transmission characteristics of the spectrometer, improvements in the analytical procedure, and identification of some of the bias components necessary for precise and accurate isotopic measurements. The development of a "Z" lens source made a further reduction of sample size by at least a factor of three feasible but was rejected to keep this parameter constant for all uranium SRM measurements.

Calibrated micro-pipettes were not used to measure the volume of solution placed on each sample filament because of the greater probability of sample cross contamination and the increased cost and time involved in sample mounting. Uncalibrated, throw-away pipettes are prepared from 5 mm pyrex glass tubing, are thoroughly cleaned, and are considered to be quick, inexpensive and safe with respect to cross contamination. The chief disadvantage of the uncalibrated pipette is visual determination of drop size, and the inability to precisely reproduce the required volume of solution for each filament, or between different sample loadings. Variation in the volume of solution is believed to be large enough to cause a 25 percent variation in the total sample size. With the relatively large amount of uranium used for an analysis (∿200 μg), this variation is not critical and the effect was less than 0.05 percent of the ratio at the 95% C.L. [9]. Figure 4 shows the tip of a throw-away pipette after depositing a drop of solution on a sample filament. Figure 5 is a close-up of the sample after conversion to the yellow oxide of uranium.

For years the volume of solution deposited on a filament was estimated to be 1/50 of an ml or approximately 20 micrliters. Using this guideline each drop of solution from a 5 mg U/ml solution contained 100 μg of uranium. Recent calibration of the drop size with a calibrated micro-syringe indicated the volume of solution was approximately 15 micro liters and the estimated quantity of uranium per drop was 75 μg. This evidence strongly indicated that all previous estimates of the amount of uranium per analysis was more of an upper limit and a better average estimate was 150 μg.

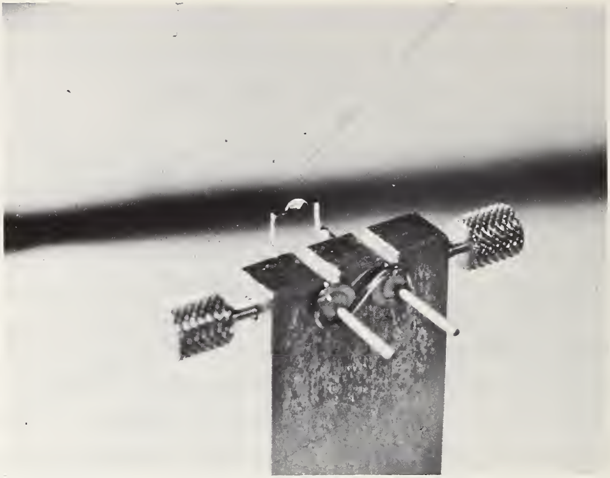

Figure 4. Deposition of solution on a sample filament.

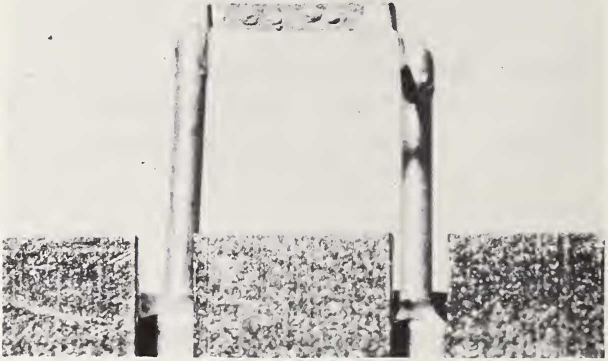

Figure 5. The yellow-orange oxide of uranium on a sample filament.

E. Time

Because of preferrential evaporation and ionization, the isotopic composition of the uranium on the sample filaments is continuously changing. The change in composition is also reflected in the ratio of $^{235}U/^{238}U$ ion currents detected at the collector. A plot of the observed $^{235}U/^{238}U$ ratio versus time over several hours of heating and under controlled analytical conditions gave a fractionation curve with a measurable slope. When sample filament temperature and sample size were variables, a series of curves with different slopes was obtained. When these two parameters were constants for all analyses, a series of curves was obtained with approximately the same slope. In general the shape of the fractionation curve is a characteristic of the temperature, time and sample size parameters used. The ratio of the light (^{235}U) to heavy (^{238}U) isotope decreased with time and was not reversible once heating of the filament was commenced.

F. Sample Mounting

The method of depositing a drop of solution on a filament and converting it to the desired form is discussed as a parameter because of the potential of unwittingly effecting a net reduction in sample size. The objective of the mounting procedure is to efficiently convert uranyl nitrate to the oxide and to bind the sample to the filament so that it does not fall or flake off. Uranium oxide (UO_3) is a preferred sample form since it is more refractory than uranyl nitrate and is not depleted from the filaments as readily.

Conversion to UO_3 was performed in a fume hood. The magnitude of the electrical current used to heat the sample and the final coloration of the sample were monitored to determine the effectiveness of the process. The sample was subjected to the cooling effect of airflow which was dependent upon the degree of cleanliness of the absolute filter and the position of the hood door. The electrical current necessary to convert the sample fluctuated in direct relationship with the volume of airflow and made current readings nothing more than a coarse indicator. The fine adjustment was to heat the sample until the color of the oxide was observed to change to a yellow-orange.

Failure to efficiently convert to uranium oxide meant that a significant portion of the sample was the more volatile uranyl nitrate and was evaporated from the filament in significant amounts at temperatures less than 1200 °C. The remaining uranium oxide sample could be abnormally small and the net result would be a probable increase in the rate of change of the isotopic ratios with time. Drying the sample too quickly or heating it too hot usually produced poor contact between filament and sample which invariably flaked off when subjected to either mechanical or thermal shock. At the conclusion of the mounting procedure filaments were inspected to ascertain if there was any migration of solution to the ends or reverse side of the filament away from the ionizing filament.

G. Total Sample Composition

Solutions of uniform and high chemical purity are essential for accurate determination of the absolute isotopic abundance of any element. High concentrations of impurities require an increased sample filament temperature to obtain the standard signal intensity for an analytical procedure. The increased sample filament temperature can be a source of bias when comparing or pooling data from the analysis of samples of variable chemical purity. Frequently, this type of temperature compensation was small and not always detected by the analyst but the net effect was usually a decrease in analytical precision of the measurement.

Once contaminant ions are identified, chemical processing will normally reduce the concentration below the critical level. For uranium analysis sodium and potassium were the major interferring elements and, although normally present in only trace quantities, required special precautions to maintain below the critical level. Sodium and potassium were also constituents of the rhenium ribbon and the filament post. Degassing prior to analysis in the mass spectrometer was used to reduce the concentration of these elements below the critical level that produced interference.

Potassium is also the source of a polymer (K_6) which produced background peaks at mass 234 and 236. When present the background peaks produced broad bases and abnormally sloped peak tops for ^{234}U and ^{236}U. With adequate precautions to maintain a minimum potassium concentration in the uranium solutions, and degassing of filaments, the potassium polymer was not detected at a 1×10^{-15}A ion current sensitivity.

Suspected organic peaks were occasionally detected during the sample degassing phase of an analysis at an ion current intensity of approximately 2×10^{-15}A. After a brief cooling and pumpdown period, organic peaks were not detectable with an ion current sensitivity of 1×10^{-15}A. Organic peaks were observed when high gain ion multipliers were used. This background was persistent and was not degraded below the detection level of the multiplier over extended periods of heating when ionizing filaments were operated at 2160 °C. Reducing the ionizing filament temperature below 2000 °C reduced the background below the detection limit of the multiplier.

H. Acidity

Isotopic analysis of uranyl nitrate dissolved in water revealed that a significant number of these samples were "hard" to analyze and required higher sample filament temperatures to obtain the standard signal intensity. Operation at the higher temperatures produced an increased rate of fractionation which resulted in a systematic difference in the data for "hard" solutions. This error term was estimated to be as large as 0.25 percent and was eliminated by adjusting all solutions to a constant acidity. With a constant acidity all samples were "hard" to analyze and responded uniformly without any detectable systematic temperature differential between samples.

After specific analytical procedures were developed, the effects of variable acidity and sample size were evaluated under low temperature and high temperature signal conditions. SRM U-500 was used as a working standard and was prepared in a nearly neutral solution (nitric acid solution evaporated to dryness on a steam bath and dissolved in water) and in acid solutions of 1, 5 and 10 percent [9]. Statistical analysis of the data revealed no systematic differences for the acid solutions as large as 0.05 percent at the 95% C.L. There was a small (<0.1%) systematic difference between the nearly neutral solutions and acid solutions analyzed under low temperature signal conditions.

The work on uranyl nitrate dissolved in water established the need for the acidity to be constant for all solutions and was reinforced by the experiment under controlled analytical conditions. For the certification analysis of the uranium SRMs, the U_3O_8 was dissolved in nitric acid (1+1) and diluted to a final concentration of nitric acid (1+19).

I. Filament Material

Rhenium was the only filament material used for uranium analysis. Rhenium was preferred to tungsten and tantalum because of a higher ionization efficiency and a lack of uranium background which was not detected at a 10^{-15}A ion current sensitivity. The material was prepared to be especially "free" of organics and the alkali elements but there were always detectable ion currents of sodium and potassium. The background of the filament assembly was further reduced before use in the spectrometer by degassing for a minimum of one hour in a vacuum and under a potential field. Failure to apply a potential allowed the contaminants to remain in the immediate volume of the filament and the cleaning process was inefficient.

The surface tension of a cleaned filament was reduced and solutions migrated to the edges, ends, and reverse side of the filament before drying. Thus, only limited degassing of the sample filaments was beneficial. After the sample was inserted into the spectrometer, the filament and sample were heated for a total of 45 minutes as part of the analytical procedure before data were taken. This final heating step was sufficient to insure insignificant background contribution from the sample or filament.

J. Pressure

Early in the development of the uranium analytical method samples subjected to overnight pumpdown frequently required abnormally high sample filament temperatures or a brief period of overheating to produce the same standard signal intensity as samples with only several hours of pumping. This temperature differential between samples was the source of a small but significant bias component which was reduced by installing a cryogenic pump (liquid nitrogen coldfinger) in the source housing. The cryogenic pump made it possible to achieve a more uniform vacuum between samples and, after a short pumpdown (<1 hour), to obtain vacuums comparable to overnight pumpdown.

Subsequent to the introduction of the source cryogenic pump, the flight tube was modified to include a beam valve [11]. The beam valve made it possible to isolate the flight tube and eliminated the regular venting to atmosphere in order to change the sample in the source housing. Except for sample degassing and the isotopic analysis, the flight tube was isolated and was maintained at a pressure of 10^{-9} torr. Near the end of the uranium program and during the analysis of SRM U-0002 it was observed that under normal operating conditions, the collector vacuum was improved to the extent that the mean free path of scattered electrons was long enough to produce baseline interference of a few parts per hundred thousand of the major peak. This interference was a significant part of the ^{235}U peak height but was not detected during degassing and was not a problem during previous uranium analyses. The interference was eliminated by devising a procedure to complete the ratio measurement before the collector vacuum could become too high.

K. Non-ohmic Response

Vibrating reed input resistors of 10^{11} ohms exhibited a non-ohmic response for ion currents significantly greater than 5×10^{-11}A and became the source of an intensity dependent bias component. The standard operating procedure to eliminate the problem was the use of a 10^{11} ohm input resistor for ion currents less than 5×10^{-11}A and switch to a 10^{10} ohm input resistor for ion currents significantly greater than 5×10^{-11}A. The 10^{10} ohm resistors eliminated non-ohmic response as a major bias component but reduced the amplified output of the VRE by a factor of 10. For some isotopic distributions, unless a compensating increase in the total signal intensity was made, the reading error in determining peak heights significantly limited the precision of the measurement.

L. R-C Response

R-C response of the measuring circuit is a source of bias when comparing large ion current ratios (>20). It was not identifiable for an ion current ratio of 20, but was detectable for a ratio of 30 and became more pronounced as a ratio of 200 was approached. When switching from a 10^{-10}A to a 10^{-13}A ion current and allowing several seconds for the circuit to stabilize, the R-C response component was at least 0.3 percent of the small peak height. Failure to fully recover would result in an apparent enrichment of the smaller isotope and without adequate calibration standards such data would be biased significantly. Sufficient data was accumulated to prove that the measuring circuit did stabilize within 30 seconds and the recovery was more than 90 percent complete. Even with calibration standards it was necessary to change from the normal cycle of equal 30 second observations per peak for $^{235}U/^{238}U$ measurements to a cycle of 30 seconds for the major peak and 60 seconds for the minor peak. The first half of the 60 seconds observation was for the measuring circuit to stabilize and the remaining half was used for data. Although the accuracy improved with sufficient time for the measuring circuit to stabilize, the precision did not reflect it. Because of the longer time intervals there was some difficulty in aligning peak tops to determine average peak heights unless the ion current emission was nearly linear.

When mass scanning to compare the minor isotopes to either ^{235}U or ^{233}U a minimum separation of 45 seconds between peak tops was maintained to minimize the effects of R-C response. The ^{235}U peak was quickscanned (∿2 seconds) during isotope dilution analyses to avoid the full effect of a large ^{235}U ion current on the Faraday cage. For this type of analysis the ^{235}U intensity was maintained below the level that would saturate the measuring circuit or require an abnormally longer recovery period even when it was only momentarily collected on the Faraday cage.

M. Memory

Memory or cross contamination between samples was not a significant bias component during thermal ionization analysis of uranium. Only one documented case of source memory was observed. This occurred early in the uranium program and was easily detected because the contaminant was ^{233}U and was not a constituent of the sample analyzed. No other significant indication of memory was ever detected. After the original source shield was modified to remove a "skirt" that extended over the drawing-out and discriminator plates, the chance of source memory was significantly reduced.

The standard procedure for minimizing possible memory contributions was to limit the analysis of SRMs on a source to a 20 percent ^{235}U abundance range and to clean the source after approximately 40 analyses. Further tests were made by analyzing separated isotopes on sources with a large number of SRM analyses and comparing the results with separated isotope data obtained on a cleaned source. Another technique was to analyze both separated isotopes on the same source and compare the data with results from a cleaned source. The final conclusion was that under normal operating conditions source memory was not significant.

5. MASS SPECTROMETRIC ANALYTICAL METHOD

A. Introduction

Because the light isotope is preferentially depleted from a heated filament and since the isotopic composition is continuously changing, it is necessary, for precise and accurate isotopic composition measurements, to approximate the same fractionation curve and the same point in time on the curve for each analysis. Under these restraints all ratio measurements are made over the same time span for each analysis and the bias effects of fractionation are evaluated and appropriate corrections made. A fixed analytical procedure is the means of reproducing the same fractionation curve for each analysis, and it gives the parameters and procedure for obtaining a specified ion current intensity. All parameters must be accurately reproduced and the rules of the procedure strictly adhered to in order to maintain the same experimental conditions for all analyses. Failure to be consistent will have a direct effect on the observed data and is detrimental to the precision and accuracy of the ratio measurement.

The analytical method for uranium isotopic analysis consisted of sample mounting, sample degassing, and the procedure or heating pattern for obtaining ion emission for the ratio measurements.

B. Sample Mounting

The same mounting procedure was used for all SRMs. One drop of solution (75-100 μg of U) was placed on each sample filament and evaporated to dryness with a heat lamp and an electrical current. The electrical current was adjusted in the following manner: 1 A for 5 minutes; 1.3 A for 3 minutes; slowly increased until the yellow-orange oxide forms (between 1.8-2.3 A).

Rapid evaporation of the solution usually produced poor contact between filament and sample. Under these conditions significant amounts of material flaked off when subjected to mechanical shock. Overheating of the sample produced a black uranium oxide which was judged to be inferior in performance to the yellow-orange oxide. Overheating also produced weak contact between the filament and the sample which resulted in material flaking off when the sample filaments were operated at high temperature (1400-1600 °C).

The sample filaments were placed into the filament block with an ionizing filament and alignment was made visually. The ionizing filament was centered in the block and the sample filaments were moved away (0.005-0.010 inch) from the edges of the ionizing filament. The completed assembly was inserted into the mass spectrometer and pumpdown commenced.

C. Degassing

Each sample was degassed for 15 minutes and then allowed to cool for a minimum of 30 minutes before the analysis was begun. When the source pressure was less than 3×10^{-6} torr, liquid nitrogen was added to the source coldfinger and degassing was accomplished in the following manner: adjust the ion accelerating voltage to 8 kV; adjust the ionizing filament temperature to 2160 °C and set the sample filament currents at 1.5 A. After 3 minutes of heating readjust the ionizing filament to 2160 °C and set the sample filament currents at 1.9 A. All filaments are turned off after a total of 15 minutes of heating. The ^{187}Re signal at the start of degassing was approximately 1.4×10^{-11}A and decaying. The initial surge of volatile material from the sample and filaments made an ion accelerating voltage of 10 kV prohibitive because of the greater frequency of high-voltage breakdowns.

Degassing dehydrated the sample and depleted the filaments of interstitial oxygen which were sources for formation of significant oxide ions (UO^+). Once the oxygen background was depleted, a significant UO^+ ion beam was not observed unless there was an air leak in the system. Initially, the U^+/UO^+ ratio was small, but the UO^+ intensity decayed much faster than the U^+ ion current and was normally less than 10^{-13}A within 10 minutes of heating. If U^+ ion currents were not degradeable to the 10^{-12}A range during degassing, it was taken to be an indication of incomplete or inefficient conversion of uranyl nitrate to the oxide. Apparent failure to deplete the filaments of unconverted uranyl nitrate was a critical indicator and was cause to terminate the analysis.

Degassing was also helpful in the degradation of potassium, sodium, and organic materials below the critical level that could cause interference. Organic background peaks were not measurable and were difficult to detect because their intensity was approximately the same as the 1×10^{-15}A background noise of the measuring circuit. Degassing followed by a brief period of source cooling and pumping, reduced low level irregularities in the baseline below the detection limit of the spectrometer. The critical check for organics was made during the first 30 minutes of an analysis and, if suspected organic peaks were observed, the analysis was terminated.

D. Analytical Procedures (Heating Pattern).

Two specific heating patterns were developed to obtain standard ion current intensities for uranium ratio measurements. The low temperature and high temperature procedures have been described previously [9] for instruments without "Z" optics. Since publication of this report, both procedures were modified to include use of an optical pyrometer to determine ionizing filament temperatures, and the high temperature procedure was changed to take into account the increased transmission of the "Z" source. Because of the wide isotopic distribution of uranium SRMs, it was impossible to operate at two standard ion current intensities and obtain maximum precision for each SRM. A general procedure was developed and is flexible enough to be used over a wide range of isotopic distributions and sample sizes (1-400 μg).

1. Low Temperature Procedure

The low temperature analytical procedure was developed and used primarily for ^{235}U/^{238}U ratio determinations of SRMs U-930 to U-050. A total ion current of approximately 3×10^{-11}A was sufficient to make expanded peak height determinations with the desired precision. When the "Z" lens source became standard on all mass spectrometers in the laboratory, the options were continued use of the old procedure or development of an equivalent procedure for the "Z" source. Both types of low temperature procedures were successfully used, and it was finally decided that the original procedure offered the best chance of maintaining the sample filament temperatures well within the desired limits (from $\sim$1200 °C to <1400 °C). Thus, the procedure described in this section is basically the same as was previously reported.

Details of the low temperature procedure are:

Time from start (minutes)	Procedure
0-1	The ionizing filament temperature is adjusted to 2160 °C and the sample filament currents are set at 1.5 A. The ^{187}Re peak is located and focussed (course) for maximum intensity. The ^{187}Re is normally $1.5\text{-}1.8\times10^{-11}$A and decaying. The stability of the rhenium signal is considered critical and, if unstable or erratic, the analysis is terminated. The most probable causes of an unstable signal are a defective filament, large alkali background, or electronic instability, etc.
5	The ionizing filament temperature will normally drift downward approximately 20 °C and is readjusted to 2160 °C.

Time from start (minutes)	Procedure
6	The sample filament currents are increased to yield a 1×10^{-11}A (100 mV) U^+ grid signal. The focus controls are adjusted for maximum intensity.
12	The sample filament currents are increased to yield a 2×10^{-11}A U^+ grid signal.
17	The ionizing filament temperature is checked to verify stabilization at 2160 °C and, if necessary, adjustments are made.
18	The sample filament currents are increased to yield a 3×10^{-11}A U^+ grid signal.
19	The U^+ signal is focussed for maximum intensity.
24	If the U^+ grid signal intensity has changed significantly ($\pm5\times10^{-12}$A), the sample filament currents are readjusted to yield 3×10^{-11}A. The uranium mass range is scanned to determine baselines.
30	The ratio measurement is started. The U^+ grid signal is expected to be approximately 3×10^{-11}A and growing slowly. Ten peak sets of data are taken by magnet switching between peak tops. Each peak top is monitored for 30 seconds except for measurement of ion current ratios greater than 20. Then the observation cycle is changed to 60 seconds for the small peak and 30 seconds for the large peak. One half of the longer observation is allowed for recovery from R-C response effects and the latter half is used for data. The measurement is concluded with a mass scan to determine baselines.

2. High Temperature Procedure

The high temperature procedure was developed to provide large U^+ ion currents to make precise determinations of minor isotope composition. The procedure is specifically designed for an internal normalization using the $^{235}U/^{238}U$ ratio of uranium as a known to evaluate bias effects for each individual analysis. The chief prerequisite is an accurate value for the $^{235}U/^{238}U$ ratio and realization that this ratio and the ratios to be corrected must be of the same magnitude or in the same response region of the measuring circuit. Also at ion current intensities of 10^{-10}A a constant awareness of non linear responses of the measuring circuit must be maintained, and adequate precautions taken to reduce their effect on the data.

Thus, the first step in determining the isotopic composition of a uranium sample is to use the low-temperature procedure, where applicable, in a separate experiment to obtain an accurate value for the $^{235}U/^{238}U$ ratio. Then the high temperature procedure is used in another experiment to determine ^{234}U and ^{236}U abundances. The best method of evaluating the filament bias for the minor isotope measurement is an internal normalization using the $^{235}U/^{238}U$ ratio as a known. This technique is a very precise and sensitive method of correcting for bias effects since a correction is made for each analysis according to its position on the fractionation curve. For an internal normalization some of the analytical control procedures and parameters, such as time, can be relaxed and the loss in precision in the average bias correction between analyses does not effect the corrected data.

The alternative technique for evaluating filament bias is to analyze a standard of known $^{235}U/^{238}U$ ratio and the sample to be calibrated under identical experimental conditions. The observed $^{235}U/^{238}U$ data of the standard is used to calculate correction factors which are applied to the observed data for the unknown sample to obtain corrected values for the isotopic composition. In contrast to internal normalization, there must be strict adherence to the rules of the analytical procedure or there will be a serious loss in precision in determining the average filament bias correction which has a direct effect on the corrected isotopic composition.

Details of the high-temperature procedure are:

Time from start (minutes)	Procedure
0-1	The ionizing filament temperature is adjusted to 2160 °C and the sample filament currents are set at 1.5 A. The ^{187}Re is normally $1.5\text{-}1.8\times10^{-11}$A and decaying. The stability of the rhenium signal is considered critical and, if unstable or erratic, the analysis is terminated. The most probable causes of unstable signals are a defective filament, a large alkali background, or electronic instability, etc.
5	The ionizing filament temperature will normally drift downward approximately 20 °C and is readjusted to 2160 °C.
6	The sample filament currents are increased to yield a 1×10^{-10}A U^+ grid signal. The focus controls are adjusted for maximum intensity.
12	The sample filament currents are increased to yield a 2×10^{-10}A U^+ grid signal.
17	The ionizing filament temperature is checked to verify stabilization at 2160 °C and, if necessary, adjustments are made.
18	The sample filament currents are increased to yield a 3×10^{-10}A U^+ grid signal.
19	The U^+ grid signal is focused for maximum intensity.

Time from start (minutes)	Procedure
24	If the U^+ grid signal intensity has changed significantly ($\pm 3\times10^{-11}$A), the sample filament currents are readjusted to yield 3×10^{-10}A. The uranium mass range is scanned to determine baselines.
30	The ratio measurement is started. The U^+ grid signal is expected to be approximately 3×10^{-10}A and slowly decaying or growing. *Seven peak sets of* $^{235}U/^{238}U$ *are taken first, by magnet switching between peak tops. Each peak is monitored for 30 seconds except for measurement of ion current ratios greater than 20. Then the observation cycle is changed to 60 seconds for the small peak and 30 seconds for the large peak. One half of the longer observation is allowed for recovery from R-C response effects and the latter half is used for data.* *Then* ^{234}U *and* ^{236}U *are compared with a reference peak of* ^{235}U *or a known* ^{233}U *spike by continuous mass scanning which is necessary for accurate measurement of baselines under the small peaks. The scan rate is adjusted to yield a minimum of 45 seconds between peak tops to minimize the effects of R-C response. Ten peak sets of minor isotope data are taken.* *Finally the ratio measurement is concluded with another 7 peak sets of* $^{235}U/^{238}U$ *data. The* ^{235}U *and* ^{238}U *baselines are determined by mass scanning.*

3. Outline of General Analytical Procedure

Because of the different isotopic distributions of the SRMs and the desire to operate with a maximum precision, analytical procedures that would yield intensities other than 3×10^{-11}A or 3×10^{-10}A were necessary. Both the low and high temperature procedures follow a general analytical pattern that is flexible and adaptable to a wide range of signal intensities The general outline for most uranium isotopic measurements is as follows: adjust the ionizing filament temperature to 2160 °C; after 6, 12, and 18 minutes of heating adjust the sample filament currents to yield 1/3, 2/3 and full intensity, respectively; focus for maximum intensity after 7 and 19 minutes of heating; verify the stability of the ionization filament temperature at 2160 °C before the final sample filament adjustment is made; after 24 minutes of heating and when necessary, reset the sample filament currents to yield full intensity. The ratio measurement is started after 30 minutes of heating. Baselines are determined by mass scanning at the beginning and end of each ratio measurement.

The general guideline in selecting a procedure for the isotopic analysis of uranium samples is to fit the procedure to the isotopic abundance ratios so that the ion current intensity is sufficient to provide the maximum precision in determining peak heights, without exceeding the limit for non-ohmic response of the measuring circuit. Hence, linearity of the input resistor is a limiting factor in determining how much signal is to be used for a ratio measurement. The other limit on the signal intensity is the ability of the collector to adequately suppress secondary electrons when a large ion beam impinges on collector surfaces. Ion current intensities of 10^{-9}A are available from a 200 μg uranium sample size but meaningful measurements at this intensity are difficult for most of the SRMs because of non-ohmic response and the bias effects of scattered electrons. Since obtaining sufficient signal intensity is not a major problem, the rate of fractionation is the next factor to be considered. Once the precision requirements for peak height determination are satisfied and adequate attention is devoted to possible non-linear effects, the best procedure is the one that yields the smaller rate of fractionation.

Since the characteristic bias of both basic procedures were well known, these procedures were used as known points of departure for obtaining ion current intensities other than those associated with the basic procedures. Therefore, selecting a procedure to fit a particular isotopic distribution was essentially modifying one of the existing procedures by obtaining either more or less than normal intensity. The only parameter that was changed to obtain a given ion current intensity was the sample filament temperature. Once the magnitude of the ion current intensity was fixed, temperature adjustments were always made according to the restraints of the general procedure described above. The advantage of this technique was the ability to predict the direction of change of the filament bias and also its approximate magnitude. Thus, a modification of the low temperature procedure to provide approximately $6\text{-}7\times10^{-11}$A of ion current would require an increase in sample filament temperature which would produce an increased rate of fractionation. At the higher rate of fractionation and with all other parameters constant, the filament bias was less than the normal low temperature bias of 0.45 percent. Under these conditions, and knowing the bias for high temperature conditions, it was possible to accurately predict a bias of between 0.4 and 0.3 percent for the modified procedure.

The basic procedures have been discussed along strict functional lines of low temperature for ^{235}U/^{238}U ratios and high temperature for minor isotopes but these procedures are not restrictive in application. When the ^{235}U abundance is greater than 95%, minor isotope determinations are usually made with a modified low temperature procedure to limit the magnitude of the ^{235}U ion current and to avoid non-ohmic response of the input resistor or saturation of the amplifier circuits to the extent of not recovering in time for minor isotope detection. Also, the high temperature procedure can be used for $^{235}U/^{238}U$ ratio measurements with approximately the same precision as the low-temperature procedure.

E. Role of the Operator in the Analytical Method

A direct comparison of isotopic data for multiple analysis of a single sample or for analyses of many different samples is meaningful and valid, only if all analytical parameters are identical or maintained within experimentally established limits, where the effect of a variation is known or is of little influence on the measurement. The task of the operator is to provide the necessary quality control to insure that each analysis falls within the prescribed analytical specifications. To accomplish this task it is necessary to verify the correctness of instrumental parameters, make a judgement as to the normalcy of the ion emission and stability, recognize and detect instrument malfunctions, and avoid procedural errors that could effect the precision and accuracy of the ratio measurement. Although the operator may give the utmost in care and attention to remain within the constraints of the procedure, a significant but small percentage of all uranium analyses will deviate from the normal pattern and must be terminated. Termination of an analysis is made by the operator as soon as it is determined that the analysis is abnormal or that an unspecified or improper adjustment has been made. Termination or rejection is always made before isotopic ratios are calculated. If the ratio is calculated, it must be accepted along with all other data until a sufficient number of analyses are made to define the limits for the experiment. If the limits are inadequate the entire series of measurements is repeated.

When the operator performs ideally and accomplishes his task, he is merely an appendage of the instrument and does not significantly increase the confidence limits of the measurement. When the operator performs poorly or unsatisfactorily, not only are the confidence limits expanded but the operator is likely to become the limiting factor in the measurement. Thus, a large number of man-hours invested in chemistry and instrumentation are negated by a failure to be consistent or reproduce the same experimental conditions for all analyses.

F. Precision of the Analytical Procedures

The extensive development of the low and high temperature procedures resulted in a degree of refinement that allows these procedures to be used as reference techniques to evaluate mass spectrometric instrumentation and also as a performance evaluation in training an operator. The bias correction for both procedures is reproducible to within 0.03 percent under controlled analytical conditions.

After a new mass spectrometer is assembled, the first analytical measurement series is a determination of the $^{235}U/^{238}U$ ratios of SRMs U-050 through U-930. This series of measurements has been designated as a systems calibration and is performed for each new or rebuilt 12-inch radius of curvature instrument before it is used for any other isotopic measurements. The systems calibration tests the linearity of the measuring circuit over a wide range of isotopic ratios by evaluating the filament bias with a fixed analytical procedure. The low temperature procedure was the preferred and most used for the systems calibration because of the lower rate of fractionation. Since the only bias measureable, over the ratio range of 20 to 0.05, is a known constant for the low temperature procedure and is due to fractionation effects in the evaporation and ionization process, analysis of these SRMs will quickly reveal any systematic error contributions from the measuring circuit.

Once a systems calibration has been performed on a mass spectrometer, the instrument is then available for general isotopic analyses and is also useful to evaluate the performance of a trainee in using a procedure for isotopic analysis. All assigned personnel of the Analytical Mass Spectrometry Section who regularly use an instrument for isotopic analysis and all trainees or guest workers are required to successfully complete the systems calibration before attempting extensive analytical programs for other elements. Thus, the characteristic filament bias of the analytical procedure becomes a reference point and the operator must learn how to accurately reproduce the exacting conditions of the procedure for every analysis. When an operator makes the initial attempt to follow the instructions of a fixed procedure, there may be some minor and unavoidable differences in what he is doing and what the specifications of the procedure are requesting. These differences are frequently systematic *i.e.* consistent use of a slightly different filament temperature, sample size or time span for completing the ratio measurement. Procedural variations of this nature may yield a systematic difference between the data of the operator and the known bias of the analytical procedure. These differences are usually small (<0.05%) for uranium analysis and are gradually reduced as the operator gains more experience with the mechanics of the method. Although the low temperature procedure was preferred for making the systems calibration, other procedures are valid and were used. The high temperature technique and an "intermediate" technique with biases of 0.2 and 0.3 percent, respectively, were used. Also, a systems calibration was made using a 40 μg sample size instead of the normal 200 μg sample size. Regardless of the type procedure selected for the systems calibration, nearly constant use of this procedure is recommended because it equates all instruments and operators to the same reference point at a precision of a few parts in ten thousand.

When the objective of an experiment is to determine the absolute abundance ratios of a sample or a group of samples, more freedom is allowable for systematic differences in procedure between operators or between experiments, as long as these differences are reproduced for each operator or for each experiment. If these differences are allowed, a correction factor must be experimentally determined by each operator and for each experiment. Different sets of parameters are allowable since the bias correction is due to fractionation effects and, if each set of parameters is precisely reproduced as a set of constants, the abundance ratios will be averaged at fixed points on different fractionation curves. But as long as known calibration standards are available and are analyzed under the same experimental conditions as all the samples in the same experiment, accurate corrections for differences in fractionation between two different experiments can be made and the corrected data should fall within the experimental limits referenced to absolute. Thus, it is practical and possible to make isotopic measurements without insisting upon reproducing the exact procedure for each experiment or that each operator obtain the same correction factor.

6. ABSOLUTE $^{235}U/^{238}U$ ABUNDANCE RATIOS OF URANIUM SRMs U-970 THROUGH U-005

A. Introduction

Absolute isotopic abundance studies by the Analytical Mass Spectrometry Section of the National Bureau of Standards include silver [16], chlorine [17], copper [13], bromine [18], chromium [15], magnesium [14], lead [19], boron [5] and rubidium [6]. Exclusive of boron and lead, where sets of 2 and 3 SRMs were certified, the end product was a single standard with an accurately known isotopic composition and atomic weight. In all of these studies it was possible to make a complete set of isotopic measurements in a relatively short time span.

The goal of the uranium isotopic program was to determine the absolute isotopic composition of 18 samples that were to be certified as SRMs. These SRMs were established by the Atomic Energy Commission (AEC) to serve as quality control standards within the AEC complex. Uranium SRMs are available to AEC contractors, AEC or state licensees, and foreign governments which have entered an Agreement for Cooperation with the U.S. Government concerning the Civil Uses of Atomic Energy. Because of significant variation in nature [20,21,22,23,24,25, 26,27,28] and the wide range of isotope distributions from man made processes, a well characterized set of uranium standards that are available to meet the needs of commercial suppliers of uranium are essential and invaluable. Since this is the most extensive set of isotopic standards with known absolute isotopic compositions for any element, they are finding increased use in evaluating and calibrating mass spectrometric measuring circuits.

The isotopic measurements were completed over an extended period as a series of independent self contained experiments, until the data was acquired for all 18 SRMs. The general experimental approach was to determine the absolute $^{235}U/^{238}U$ ratio using synthetic calibration mixes of known isotopic composition and then in a separate experiment determine minor isotopic composition by ^{233}U isotope dilution. With these bits of information, the smaller of the major isotopes (^{235}U and ^{238}U) was calculated directly and the composition of the remaining isotope was determined by difference.

The only measurable bias was the temperature and mass dependent fractionation factor related to the ionization process in the source. Thus, for the instruments used in this study, it was necessary to demonstrate that a single correction factor was valid over a wide range of isotopic ratios. Calibration mixes prepared from nearly pure separated isotopes of ^{235}U and ^{238}U were used to evaluate the bias factor at $^{235}U/^{238}U$ ratios of 10, 1, and 0.1. The bias was a constant, within experimental error, when the samples were analyzed under identical experimental conditions. By significantly changing the heating pattern or increasing the sample temperatures, the magnitude of the bias was changed, but it was a constant for each set of identical experimental conditions. The data for the low temperature and high temperature procedures are given in Table 7.

B. Experimental Procedure

1. Mass Spectrometry

Isotopic measurements of the calibration mixes and the SRM samples were made on three different single-stage solid-sample mass spectrometers. Each instrument had a 12-inch radius of curvature 68° analyzer tube and 60° sector magnet and was equipped with the expanded scale-measuring circuit, the NBS collector, source coldfinger, and triple filament rhenium ribbons (0.001×0.030 inch) in the ion source.

The sample filaments were prepared for mass spectrometric analysis according to the sample mounting procedure of Section 5,B. An ion accelerating voltage of 10 kV was used and ratios were determined by measuring U^+ ions. The low temperature analytical procedure or a slight modification of this technique was used for most measurements. In spite of the extended time

Table 7. Comparison of the calculated $^{235}U/^{238}U$ ratio to the observed $^{235}U/^{238}U$ ratio for low and high temperature analyses of synthetic uranium samples.

		Low temperature	
Mix	Ratio of 0.1	Ratio of 1	Ratio of 10
1	0.99564	0.99584	0.99597
2	0.99523	0.99476	0.99590
3	0.99574	0.99521	0.99619
4	0.99488	0.99567	0.99585
5	0.99520	0.99563	0.99608
Average =	0.99534	0.99542	0.99600
		High temperature	
1	0.99857	0.99742	0.99780
2	0.99852	0.99795	0.99786
3	0.99786	0.99720	0.99793
4	0.99830	0.99851	0.99800
5	0.99783	0.99779	0.99718
Average =	0.99822	0.99777	0.99775

period and the many instrumentation changes the fundamental parameters for measuring ion currents were nearly the same for each experiment in the series. Because of the continuous development and upgrading of the instrumentation, a brief description of the mass spectrometer is included for each series of measurements in this Section and in Section 7. The standard procedure was to use the most advanced instrumentation available for the uranium isotopic abundance measurements.

2. Isotopic Composition of "U235" and "U238" Separated Isotopes

The isotopic compositions of the separated isotope samples were initially determined by a direct comparison with the major isotope. Then the measured ^{234}U of the "U235" sample and the ^{235}U of the "U238" sample were used as target values for a determination by isotope dilution. The isotope dilution measurements were made on a mass spectrometer equipped with an ion multiplier, and corrections for the effects of bias were made by analyzing SRM U-500 under the same experimental conditions.

The difference between the isotope dilution data and the data from comparisons with the major peak was less than 1 percent for the "U235" sample, and less than 1 ppm for the ^{235}U of the "U238" sample. The isotopic compositions as determined by the dilution technique were used as best values and the results are given in Table 8. The ^{234}U and ^{236}U isotopes were not detected in "U238" and the limit of detection was less than 1 ppm.

Table 8. Composition of "U235" and "U238" separated isotopes.

	Isotopic composition (atom percent)			
Separated isotope	^{234}U	^{235}U	^{236}U	^{238}U
"U235"	0.0442	99.8195	0.0574	0.0789
	±.0005[a]	±.0020	±.0005	±.0006
"U238"	<.0001	0.0004	<.0001	99.9996
		±.0001		±.0002

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[a] The uncertainties are 95% C.L.

3. U_3O_8 Ignition Procedure

a. Apparatus - Platinum Boats (Figure 6): The boats were formed from 20×33 mm pieces of 2 mil platinum foil. The sides were 6.5 mm high and the folds were left slightly open to prevent material from being trapped. The boats were cleaned by heating in hydrochloric acid (1+1), igniting to 1200 °C, heating in hydrochloric acid (1+1), rinsing with water, heating in nitric acid (1+1), and rinsing with water.

Glass Desiccators (Figure 6): The desiccators were made from ground glass joints to contain the platinum boats during movement and weighing. The weighings were done on a 20 g capacity microbalance so the weight of the desiccator was limited to a maximum of 17 g. A minimum of silicone grease was used as lubricant and sealer. The desiccators were cleaned in hot nitric acid (1+1) before they were used on samples with different isotopic composition.

Ignition Tube (Figure 7): A quartz ignition tube, 3 ft long, 13 mm i.d., and 15 mm o.d. was used. End pieces of glass were butt joined with plastic tubing. The front end piece was 13 mm i.d., had a side arm for air or oxygen entry, and was closed with a sealed tube attached by a ball and socket joint. The back end piece was a reducing adapter from 15 mm o.d. to 6 mm o.d. A separate quartz tube was reserved for each isotopic level and was cleaned with nitric acid (1+1) before use. The end pieces were cleaned by heating in nitric acid (1+1) before use on the next tube.

Air and Oxygen Supply: The air and oxygen supply lines were copper and glass tubing, butt joined with plastic tubing. The gasses were passed through sulfuric acid and then ascarite and magnesium perchlorate before entering the sidearm of the front end piece on the ignition tube.

Furnace (Figure 7): A tube furnace capable of continuous operation at 1050 °C was used. It was mounted on wheels to enable it to be moved back and forth over the sample area of the ignition tube.

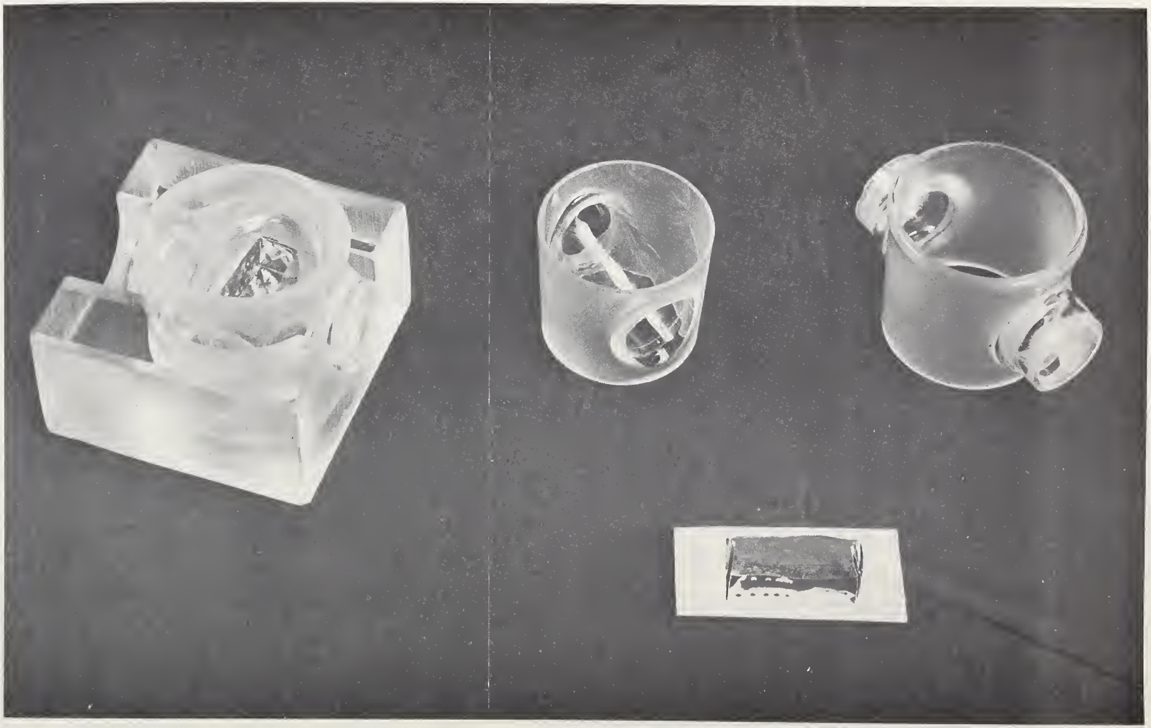

Figure 6. Platinum boat and glass desiccator used in U_3O_8 ignition.

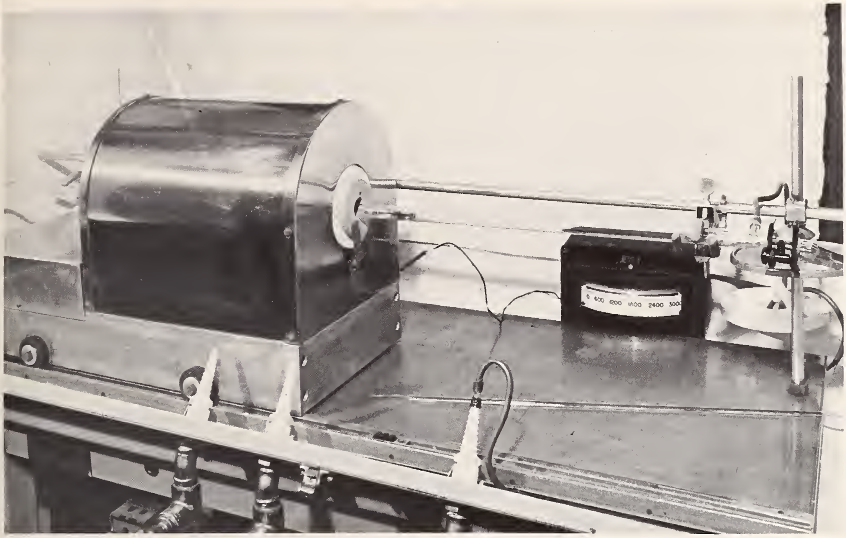

Figure 7. Furnace with quartz ignition tube for ignition of uranium oxides.

b. Procedure - The empty sample desiccator and tare desiccators, after sitting at least one hour to reach temperature equilibrium, were opened momentarily to equalize pressure in the desiccators and then placed on a grounded steel plate. After waiting 15 minutes, the sample desiccator and tare desiccators (these were weighed each time a sample desiccator was weighed) were weighed on a 20 g capacity microbalance. An empty platinum boat, ignited in the ignition tube at 1050 °C with an air flow of about 8 to 10 ml per minute, was drawn out of the tube directly into the sample desiccator. The desiccator was quickly closed and allowed to stand approximately 1 hour. The desiccator was opened momentarily and weighed as before.

The boat was removed from the desiccator and the sample of uranium oxide was transferred to the boat. (All work involving open samples of radioactive material was conducted in a glove box or hood.) After transferring the boat and sample back to the desiccator; the desiccator, boat, and sample were weighed as before.

The boat with sample was transferred to the ignition tube, the furnace was moved to cover the boat, and the sample was ignited at 900 °C for 1 hour with air flowing at about 8 to 10 ml per minute. The furnace was moved back and the sample was allowed to cool 10-15 minutes. The boat was drawn into the desiccator and weighed as before. The ignition was repeated at 1050 °C for 16 hours in air. After cooling the boat was transferred to the desiccator and weighed as before. The ignition was repeated at 850 °C for 1 hour in an oxygen atmosphere (>99%) at a flow rate of about 8 to 10 ml per minute. When the furnace had been rolled back and the sample had cooled, oxygen was turned off and air was turned on at about 10 to 12 ml per minute. After 30 minutes of air flow the sample was removed and weighed as before. After the boat and sample were removed the empty desiccator was reweighed to check for any desiccator weight change.

c. Discussion of Procedure - Glass desiccators were used to contain the samples to prevent exposure of the sample to moist air and to prevent contamination of the balance and surrounding area. The desiccators were constructed to weigh not more than 17 g, so that the combined weight of desiccator, platinum boat and sample would remain within the 20 g capacity of the microbalance used. To achieve accurate weighing to within a few micrograms several precautions were taken. The desiccators were placed on a grounded steel plate and were handled with grounded tongs, the balance was grounded and was shielded from drafts, at least 30 percent relative humidity was maintained in the room, and the balance was calibrated with NBS calibrated weights. Four desiccators were weighed with the sample desiccators so that corrections due to changes in temperature and pressure could be applied. This correction has been as large as 200 µg although it was usually less than 100 µg. The platinum boats were checked for loss on ignition at 1050 °C by heating at 1050 °C for 54 hours. They showed an average loss of less than 2 µg.

The ignition at 900 °C was done so that the sample could be compared to earlier work. On samples that had consistent ignition loses, the ignition at 900 °C and the weighing after the 1050 °C ignition were eliminated.

To establish a limit to any change in the desiccator weight it was weighed after the boat and sample were removed. A loss in weight of the desiccator could result from such things as a chip of glass broken off from the desiccator, a loss of lubricant or a loss of foreign particle which had been on the desiccator before the first weighing. A gain in weight of the empty desiccator could be due to U_3O_8 spilling from the boat into the desiccator or to foreign particles landing on the desiccator after the original empty desiccator weight had been taken. These changes in weight could result in an error in the apparent weight of U_3O_8 depending on when the weight change occured. If the change happened after the empty boat weighing and before the final sample weighing the apparent U_3O_8 weight would be in error but if it happened before the empty boat weighing or after the final sample weighing the apparent U_3O_8 weight would not be in error. Since it might or might not affect the U_3O_8 weight, one-half of the empty desiccator weight change was applied to the apparent weight of U_3O_8. This correction was very small in most cases, with the largest correction being equal to 0.004 percent.

The weight of U_3O_8 was obtained by subtracting the empty boat weight from the ignited at 850 °C in oxygen weight and making the corrections for empty desiccator weight changes.

4. Preparation of Calibration Mixes Containing $^{235}U/^{233}U$ Ratios of 9, 1 and 0.1

a. Procedure - Each sample was ignited (Section 6,B,3) using the weight of sample calculated to give the desired

$^{235}U/^{238}U$ ratio. The platinum boat and sample were carefully transferred from the desiccator to a 250 ml teflon bottle wrapped in a damp paper towel to reduce any static charge on the bottle. After both the "U235" and "U238" separated isotopes were ignited and transferred to the bottle, sufficient nitric acid (1+1) was added to the bottle to give a nitric acid (1+19) solution containing 5 mg U/ml when diluted with water. The bottle was sealed with a teflon-lined cap and heated on a steam bath for an additional 1/2 hour after all the sample had appeared to dissolve. Sufficient water was added to give a nitric acid (1+19) solution and the solution was thoroughly mixed.

b. Discussion of Procedure - These samples were prepared for point and systems calibration of the mass spectrometer. The first mixes of "U235" and "U238" separated isotopes were to bracket the SRM U-500. Five samples of approximately 0.25 g of the "U235" separated isotope were ignited and then the calculated amounts of "U238" separated isotope to give a range of $^{235}U/^{238}U$ ratios from 0.99 to 1.01 were ignited. Five mixes were prepared to allow an evaluation of the mixing procedure as well as the mass spectrometry measurement.

The solutions with $^{235}U/^{238}U$ ratios of 9 were prepared using 0.9 to 1.0 g samples of "U235" separated isotope and 0.10 to 0.11 g samples of SRM U-0002. SRM U-0002 was of adequate isotopic purity to use for these mixes. The solutions with $^{235}U/^{238}U$ ratios of 0.11 were prepared by the same procedure except for a reversal of the amounts of the "U235" separated isotope and SRM U-0002.

Teflon picks up a static charge very easily and if the charge is not discharged some of the uranium oxide may jump out of the boat onto the bottle. It has been found that a damp towel will discharge the static charge on the teflon and then the boat and sample can be safely transferred into the bottle. Approximately 200 transfers using this technique have been accomplished without any indication of a problem. All nitric acid used for the uranium samples was checked for uranium by either "U233" isotope dilution mass spectrometry or by fluorescence. The fluorescence procedure indicated less than 5 ppb U (limit of detection) in one lot of nitric acid and the isotope dilution procedure indicated less than 0.01 ppb in another lot. The samples were dissolved in nitric acid (1+1) by heating over a small steam bath in a radioactivity hood. This required from one to four hours for all visible oxide to dissolve. The samples were heated for about 30 minutes after all the visible material had dissolved to insure complete solution. The solutions were then diluted with water to give a final solution of 5 mg U/ml in nitric acid (1+19).

The $^{235}U/^{238}U$ ratio (Table 9) was calculated for each mix using the following equations:

$$\text{Calculated } ^{235}\text{U}/^{238}\text{U} = \frac{\text{Moles } ^{235}\text{U "U235" + moles } ^{235}\text{U "U238"}}{\text{Moles } ^{238}\text{U "U235" + moles } ^{238}\text{U "U238"}} \quad \{1\}$$

Moles ^{235}U "U235" = moles of ^{235}U from the "U235" separated isotope

Moles ^{235}U "U238" = moles of ^{235}U from the "U238" separated isotope

Moles ^{238}U "U235" = moles of ^{238}U from the "U235" separated isotope

Moles ^{238}U "U238" = moles of ^{238}U from the "U238" separated isotope

The moles of ^{235}U in the "U235" separated isotope were calculated by equation {2}.

$$A = \frac{BC}{D} \qquad \{2\}$$

A = moles of isotope ^{235}U from the "U235" separated isotope

B = g of "U235" separated isotope

C = atom percent of ^{235}U in the "U235" separated isotope

D = 1/3 of the molecular weight of U_3O_8 in the "U235" separated isotope

The values of the remaining isotopes were calculated in a similar manner.

Table 9. Calculated $^{235}U/^{238}U$ ratios of calibration mixes for SRM U-900, SRM U-500 and SRM U-100.

	Separated isotope		
Mix No.	"U238"[a] (g U_3O_8)	"U235" (g U_3O_8)	Calculated $^{235}U/^{238}U$
13-186	0.102246	0.923314	9.0481
13-185	0.103162	0.926991	9.0038
13-35	0.26243	0.25911	0.9954
13-36	0.27698	0.27159	0.9886
13-37	0.25841	0.25757	1.0049
13-38	0.25146	0.25206	1.0106
13-39	0.24989	0.24836	1.0020
13-177	0.911160	0.100724	0.11173
13-179	0.921865	0.101374	0.11114

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[a] "U238" separated isotope was used for mixes No. 13-35 through 13-39 and SRM U-0002 was used for the remainder.

The teflon, platinum and glass equipment such as bottles, beakers, droppers and needles used to contain uranium, water or nitric acid for all the work described in this publication, were cleaned in detergent, rinsed with distilled water, heated to boiling for at least one hour in nitric acid (1+1), rinsed with distilled water and allowed to dry.

5. Preparation by Solution Aliquoting of Calibration Mixes Containing $^{235}U/^{238}U$ Ratios of 0.005 to 0.05

a. Procedure - The "U238" separated isotope samples were ignited (Section 6,B,3), transferred to teflon bottles and dissolved as before (Section 6,B,4). The "U235" separated isotope samples were also ignited as above. A teflon bottle was wiped with a damp towel to remove any static charge, allowed to stand 1-2 minutes and weighed. The "U235" separated isotope sample was transferred to the weighed teflon bottle and dissolved in enough nitric acid (1+1) to give nitric acid (1+19) solutions containing 3 mg U/ml when diluted. The "U235" solutions were then diluted to 3 mg U/ml with water, mixed thoroughly and allowed to stand overnight before the final weight was taken. The cap of the "U235" bottle was quickly replaced with a rubber serum septum (Figure 8). A four inch platinum needle was inserted through the septum. A short second needle which just punctured the septum served as a vent. A 10 ml plastic syringe with the rubber plunger covered by a thin teflon sheet was attached to the Kel-F hub of the platinum needle and the desired amount of solution was drawn into the syringe. The needle with the syringe still attached was raised above the level of the solution and a small amount of air was drawn into the tip of the syringe. The syringe was disconnected from the hub and the tip was wiped with a dry paper towel and quickly capped with a Kel-F cap. Any static charge that might be on the syringe was dissipated by wiping it with a damp paper towel, and the syringe and contents were weighed on a semi-microbalance to the nearest 0.01 mg. The solution was delivered from the syringe to the weighed bottle containing

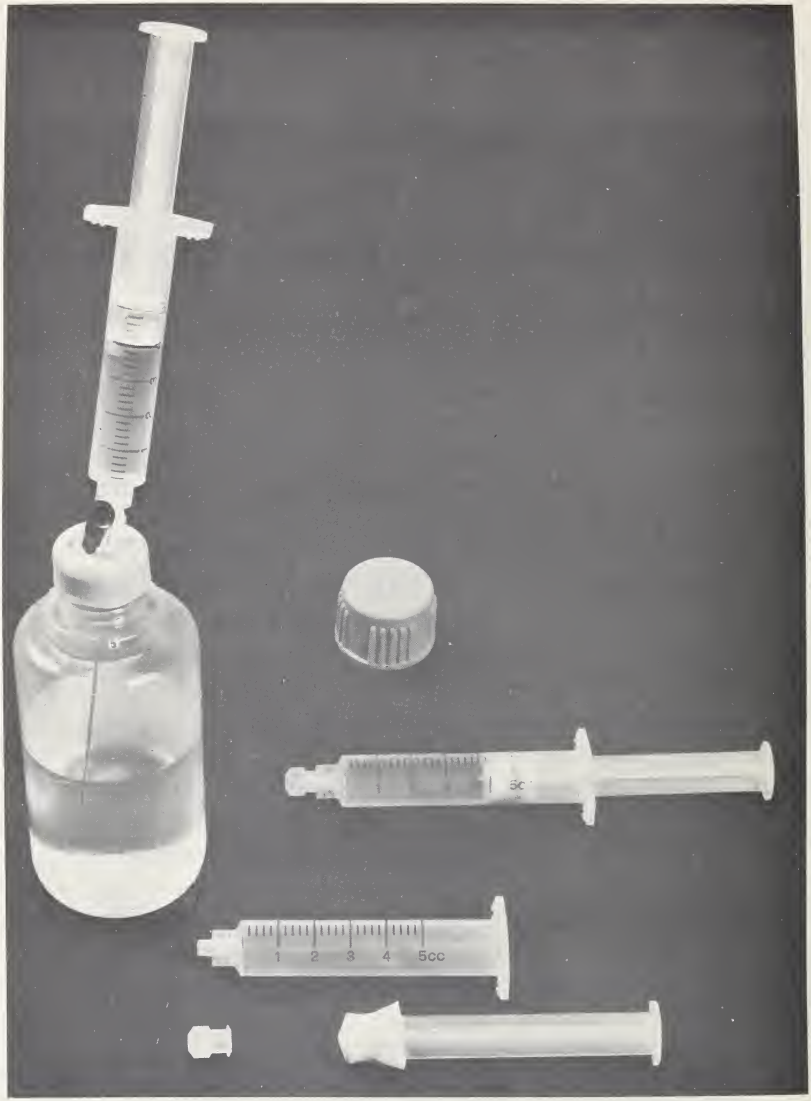

Figure 8. Apparatus used for weight aliquoting.

the "U238" sample solution. The syringe was quickly capped, then wiped and weighed again. The weight of the "U235" aliquot was determined from the weights of the syringe before and after delivery of the sample. The calibration solution was mixed, diluted with water to give 5 mg U/ml and mixed again.

b. Discussion of Procedure - These mixes were prepared for mass spectrometer calibration at the $^{235}U/^{238}U$ ratios of the six SRMs (U-005 through U-050) having less than 10 percent ^{235}U. Unless very large amounts of "U238" separated isotope were used, the amount of "U235" separated isotope needed could not be weighed directly with the required accuracy. Since the quantity of separated isotopes is limited, the "U235" isotope was added as a weighed aliquot. The "U238" separated isotope samples of 0.5 to 1.2 g were ignited and transferred to teflon bottles as before (Section 6,B,4). Two "U235" separated isotope samples of 0.30 and 0.35 g were ignited and transferred to separate weighed teflon bottles. Two samples of "U235" separated isotope were taken for greater reliability in the results. With reasonable care the possibility of an error is low, but an error in weighing, an error in recording the weight, an unnoticed loss of sample or solution, or contamination can occur. Two samples of "U238", one spiked with one "U235" solution and the other "U238" sample spiked with the second "U235" solution, were prepared to closely bracket the $^{235}U/^{238}U$ ratio of each of the SRMs.

Teflon bottles pick up static charges very easily and can cause significant apparent weight changes. On 125 ml and 250 ml teflon bottles, static charges have resulted in apparent weight changes of as much as 30 mg. It was found that by wiping the teflon bottle with a damp paper towel and allowing it to stand for 1-2 minutes the reproducibility was ±1 mg. On weighing 100 g of solution, the amount used on these samples, the error would be no more than 2 parts in 100,000 from this source. A discussion of aliquoting is given in Section 2,D.

The $^{235}U/^{238}U$ ratio was calculated using equation {1} (Section 6,B,4). The moles of ^{235}U from the "U235" separated isotope were calculated from equation {3}.

$$A = \frac{BCE}{DF} \tag{3}$$

A = moles of isotope ^{235}U in the "U235" separated isotope aliquot

B = g of "U235" separated isotope in the solution

C = atom percent of ^{235}U in the "U235" separated isotope

D = 1/3 of the molecular weight of U_3O_8 in the "U235" separated isotope

E = g of aliquot taken

F = g of "U235" separated isotope solution

The moles of ^{238}U were calculated in a similar manner. The calculated $^{235}U/^{238}U$ ratios are given in Table 10.

6. Preparation of Calibration Mixes for SRM U-970

a. Procedure - These solutions were prepared according to the procedure used for the solutions containing $^{235}U/^{238}U$ ratios of 0.005 to 0.05 (Section 6,B,5) with the "U238" separated isotope being the solution aliquoted by weight instead of the "U235" separated isotope. The "U238" separated isotope samples were diluted to approximately 1.3 mg U/ml and 5 ml plastic syringes were used to add weighed aliquots of the "U238" solution to the "U235" samples.

Table 10. Calculated $^{235}U/^{238}U$ ratios of calibration mixes for SRM U-005 through SRM U-050.

Solution No.	"U238" (g U_3O_8)	"U235" (g soln)	"U235" soln No.	Calculated $^{235}U/^{238}U$
16-144	1.009929	7.01233	1[a]	0.0209439
16-145	1.182429	5.40564	2[b]	0.0156728
16-146	1.188715	3.99410	1	0.0101372
16-147	1.204562	3.63029	2	0.0103335
16-148	1.225201	1.94921	1	0.0048020
16-149	1.255977	1.83482	2	0.0050110
16-152	0.595380	9.27539	2	0.0533976
16-153	0.985517	5.97268	2	0.0207755
16-154	1.139857	5.86156	1	0.0155123
16-159	0.592706	10.45382	1	0.0531937
16-160	0.665352	6.09923	2	0.0314218
16-161	0.624362	6.62499	1	0.0320039

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[a] "U235" solution No. 1 contained 2.52977 mg U/g of solution.

[b] "U235" solution No. 2 contained 2.87501 mg U/g of solution.

b. Discussion of Procedure - Four mixes were prepared using 0.9 to 1.0 g samples of "U235" separated isotope and two solutions of "U238" separated isotope for aliquoting. The two "U238" solutions of 103 and 106 g were prepared using 150 and 160 mg of U_3O_8. Aliquots of from 2.5 to 3.0 g of the "U238" solution were taken using plastic syringes. The $^{235}U/^{238}U$ ratios were calculated using equations {1} and {3} except the calculation was for the "U238" separated isotope in equation {3}. The values for the calibration solutions are given in Table 11.

Table 11. Calculated $^{235}U/^{238}U$ ratios of calibration mixes for SRM U-970.

Sample No.	Separated isotopes "U235" (g U_3O_8)	 "U238" (g soln)	Calculated $^{235}U/^{238}U$
17-86	0.995261	2.88470[a]	193.785
17-92	0.906216	2.67256[a]	190.956
17-93	0.922357	2.67714[b]	197.106
17-94	0.988828	2.97297[b]	191.316

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[a] This "U238" solution contained 1.29004 mg U/g of solution.

[b] This "U238" solution contained 1.26260 mg U/g of solution.

7. Analysis of Calibration Mixes and SRMs U-900, U-500 and U-100

The point calibration technique was used for each SRM in this group and consisted of using synthetic mixes blended to have $^{235}U/^{238}U$ ratios approximately the same as the SRM to be calibrated. This procedure provides an accurate means of correcting for bias of a given ratio (point) but does not yield any information about the dependency of the bias on the magnitude of the ratio.

The $^{235}U/^{238}U$ ratio of SRM U-500 was the first to be determined because all random and systematic bias components were nearly identical for each isotope. Two different operators and two different 12-inch radius of curvature 68° analyzer tube mass spectrometers were used. Five calibration mixes and the SRM were analyzed to obtain a single analysis for all samples on Instrument No. 1 and to obtain duplicate analyses for all samples on Instrument No. 2. A modified low temperature procedure was used and the U^+ ion current was approximately 5×10^{-11}A and decaying slowly. Correction factors were determined for each instrument by calculating the ratio of the "calculated" $^{235}U/^{238}U$ to the observed $^{235}U/^{238}U$. The correction factors and the absolute ratio determination are given in Tables 12 and 13.

Table 12. Correction factor for calibration of $^{235}U/^{238}U$ ratio of SRM U-500.

		Instrument No. 1		Instrument No. 2	
Calibration mix No.	Calculated $^{235}U/^{238}U$	Observed[a] $^{235}U/^{238}U$	Correction factor	Observed[a] $^{235}U/^{238}U$	Correction factor
13-35	0.9954	0.9985	0.99689	0.9993	0.99610
				0.9988	0.99660
13-36	0.9886	0.9915	0.99707	0.9914	0.99718
				0.9917	0.99687
13-37	1.0049	1.0072	0.99771	1.0086	0.99633
				1.0076	0.99732
13-38	1.0106	1.0140	0.99664	1.0136	0.99704
				1.0131	0.99753
13-39	1.0020	1.0053	0.99671	1.0055	0.99652
				1.0045	0.99751
		Average	0.9970		0.9969

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[a] Each value represents a single analysis.

Table 13. Absolute ^{235}U/^{238}U ratio of SRM U-500.

Instrument No. 1		Instrument No. 2	
Observed	Corrected	Observed	Corrected
1.0029	0.99989	1.0031	0.99999
1.0031	1.00009	1.0030	0.99989
1.0026	0.99959	1.0023	0.99919
1.0032	1.00019	1.0022	0.99909
1.0035	1.00049	1.0026	0.99949
		1.0037	1.00059
		1.0023	0.99919
		1.0027	0.99959
		1.0025	0.99939
		1.0020	0.99889
Average =	1.0000		0.9995

The absolute ^{235}U/^{238}U ratios of SRMs U-900 and U-100 were determined approximately one year after completion of the measurement for SRM U-500. The 12-inch radius of curvature 68° analyzer tube mass spectrometer was used. Two calibration mixes were prepared for each SRM and were used to determine correction factors and calibrate for the effects of bias. Two reference solutions were used for each SRM and were selected to evaluate possible differences between samples that had been dissolved for different lengths of time. Solutions labeled "A" were dissolved approximately 1 year before the measurement and solutions labelled "B" were dissolved several weeks prior to the analysis. The calibration mixes and SRM solutions were analyzed in an alternate pattern until 4 analyses were obtained for each sample. Although memory was not detected, all measurements were completed on SRM U-100, and the source was disassembled and thoroughly cleaned to further reduce any chance of memory contributions before proceeding with ratio measurement for SRM U-900. The correction factors and absolute ratios are summarized in Tables 14 and 15.

Table 14. Correction factors for calibration of $^{235}U/^{238}U$ ratios of SRM U-900 and SRM U-100.

Calibration mix No.	Calculated $^{235}U/^{238}U$	Observed $^{235}U/^{238}U$	Correction factor
	SRM U-900		
13-185	9.0038	9.04750	0.99517
		9.04628	0.99530
		9.04301	0.99566
		9.04459	0.99549
13-186	9.0481	9.09248	0.99512
		9.08780	0.99563
		9.08157	0.99632
		9.08903	0.99550
		Average =	0.99552
	SRM U-100		
13-177	0.11173	0.112149	0.99626
		0.112129	0.99644
		0.112176	0.99602
		0.112198	0.99583
13-179	0.11114	0.111579	0.99607
		0.111625	0.99566
		0.111674	0.99522
		0.111694	0.99504
		Average =	0.99582

Table 15. Absolute $^{235}U/^{238}U$ ratios of SRM U-900 and SRM U-100.

	SRM U-900		SRM U-100	
Solution	Observed	Corrected	Observed	Corrected
A	10.4249	10.3782	0.114083	0.113606
	10.4259	10.3792	0.114085	0.113608
	10.4111	10.3644	0.114081	0.113604
	10.4219	10.3752	0.114023	0.113546
B	10.4203	10.3736	0.114046	0.113569
	10.4272	10.3805	0.114058	0.113581
	10.4213	10.3746	0.114173	0.113696
	10.4194	10.3727	0.114064	0.113587
Average =		10.375		0.11360

8. Absolute $^{235}U/^{238}U$ Ratios by Interpolation

Once it was demonstrated that the bias was independent of isotopic composition for $^{235}U/^{238}U$ ion current ratios between 10 and 0.1, it was decided to determine the remaining $^{235}U/^{238}U$ ratios within this range by interpolation. The interpolation method consisted of using samples of known $^{235}U/^{238}U$ ratios to determine correction factors near the end points and at the midpoint of the ratio range to be calibrated. If both the calibration samples and the "unknown" samples are analyzed under identical experimental conditions, then a single correction factor is valid to correct all ratios within the limits of the calibration.

SRMs U-900, U-500 and U-100 were used as standards of known $^{235}U/^{238}U$ ratios and were analyzed under the same experimental conditions as the SRM samples to be calibrated (SRMs U-930, U-850, U-800, U-750, U-350, U-200, U-150 and U-050). SRMs U-930 and U-050 were included in the group although they were beyond the end points of the calibration standards.

A low temperature analytical procedure was used. Two reference solutions were used for each SRM and were labelled "A" for dissolution 1 year prior to the measurement and "B" for dissolution immediately before the measurement. Because of the wide range of $^{235}U/^{238}U$ ratios to be determined, alternate analyses of "calibration" samples with the SRMs was not practical. All samples were divided into three groups, with each group covering a maximum ^{235}U composition range of approximately 20 percent, and were analyzed in order of decreasing ^{235}U composition. The sample groupings were U-930 to U-750, U-500 and U-350, and U-200 to U-050. The source was disassembled and thoroughly cleaned for the analysis of each group. The calculation of correction factors is summarized in Table 16 and the absolute ratios in Table 17. Since there was no experimental difference between "A" and "B" solutions, this designation was not included in the Table.

9. Analysis of Calibration Mixes and SRMs U-050 through U-005

The ratio of ^{235}U and ^{238}U ion currents of this group of SRMs varied from approximately 0.05 to 0.005. Non-ohmic response and the R-C response of the measuring circuit were sources of bias that made point calibration of each SRM mandatory. A single focussing, 12-inch radius of curvature 68° analyzer tube mass spectrometer with a "Z" lens source was used. The flight tube was equipped with a beam valve and was used to isolate the tube from the source housing except during sample degassing and the analysis.

SRM U-050 was an end-point for the $^{235}U/^{238}U$ ratio determination by the interpolation method and the ratio was redetermined by the point calibration method as a tie-point between the two sets of measurements. SRM U-050 was analyzed using an equivalent low temperature procedure for the "Z" lens source. The signal intensity was approximately 5×10^{-11}A and growing. An optimum signal intensity was selected for each succeeding SRM to yield maximum precision on the expanded scale peak height

Table 16. Correction factor for calibration of $^{235}U/^{238}U$ ratios by the interpolation method.

SRM	Absolute	Observed	Correction factor
U-900	10.375	10.4278	0.99494
		10.4193	0.99575
		10.4299	0.99474
		10.4180	0.99587
			0.99532
U-500	0.9997	1.00460	0.99512
		1.00425	0.99547
		1.00422	0.99550
		1.00442	0.99530
			0.99535
U-100	0.11360	0.114118	0.99546
		0.114110	0.99553
		0.114100	0.99562
		0.114144	0.99523
			0.99546
		Average =	0.99538

Table 17. Absolute $^{235}U/^{238}U$ ratios for SRMs U-930, U-850, U-800, U-750, U-350, U-200, U-150 and U-050.

SRM	Observed	Corrected
U-930	17.4395	17.3589
	17.4331	17.3526
		17.356
U-850	6.17729	6.1488
	6.17697	6.1484
		6.149
U-800	4.28742	4.2676
	4.28803	4.2682
		4.268
U-750	3.17976	3.1633
	3.18009	3.1654
		3.164
U-350	0.548962	0.54643
	0.548858	0.54632
		0.5464
U-200	0.252293	0.251127
	0.252422	0.251256
		0.25119
U-150	0.181931	0.181090
	0.181910	0.181070
		0.18108
U-050	0.052994	0.052749
	0.053012	0.052767
		0.05276

determination. Each SRM and its corresponding calibration mixes were analyzed in an alternate pattern until there were a total of 6 analyses for the SRM sample and 6 analyses for the calibration mixes. A correction factor was calculated using the calibration mixes and was used exclusively to correct the SRM with approximately the same $^{235}U/^{238}U$ ratio. The calculation of correction factors and of absolute ratios are summarized in Tables 18 through 23.

Table 18. Absolute $^{235}U/^{238}U$ ratio of SRM U-050.

Calculation of correction factor

Calibration mix No.	Calculated	Observed	Correction factor
16-152	0.053398	0.053624	0.995785
		0.053640	0.995488
		0.053622	0.995823
16-159	0.053194	0.053385	0.996422
		0.053422	0.995732
		0.053402	0.996105
		Average =	0.99589

Absolute ratio

Observed	Corrected
0.053000	0.052782
0.053010	0.052792
0.053010	0.052792
0.052997	0.052779
0.052987	0.052769
0.052984	0.052766
Average =	0.05278

Table 19. Absolute $^{235}U/^{238}U$ ratio of SRM U-030.

Calculation of correction factor

Calibration mix No.	Calculated	Observed	Correction factor
16-160	0.031422	0.031531	0.996543
		0.031525	0.996733
		0.031526	0.996701
16-161	0.032004	0.032094	0.997196
		0.032105	0.996854
		0.032102	0.996947
		Average =	0.99682

Absolute ratio

Observed	Corrected
0.031533	0.031433
0.031535	0.031435
0.031508	0.031408
0.031515	0.031415
0.031539	0.031439
0.031531	0.031431
Average =	0.03143

Table 20. Absolute $^{235}U/^{238}U$ ratio of SRM U-020.

Calculation of correction factor

Calibration mix No.	Calculated	Observed	Correction factor
16-144	0.020944	0.021003	0.997191
		0.021015	0.996621
		0.021015	0.996621
16-153	0.020776	0.020847	0.996594
		0.020843	0.996785
		0.020843	0.996785
		Average =	0.99677

Absolute ratio

Observed	Corrected
0.020870	0.020803
0.020882	0.020815
0.020865	0.020798
0.020877	0.020810
0.020874	0.020807
0.020881	0.020814
Average =	0.02081

Table 21. Absolute $^{235}U/^{238}U$ ratio of SRM U-015.

Calculation of correction factor

Calibration mix No.	Calculated	Observed	Correction factor
16-145	0.015673	0.015721	0.996947
		0.015720	0.997010
		0.015709	0.997708
16-154	0.015512	0.015545	0.997877
		0.015564	0.996659
		0.015551	0.997492
		Average =	0.99728

Absolute ratio

Observed	Corrected
0.015610	0.015568
0.015609	0.015567
0.015612	0.015570
0.015598	0.015556
0.015609	0.015567
0.015612	0.015570
Average =	0.015566

Table 22. Absolute $^{235}U/^{238}U$ ratio of SRM U-010.

Calculation of correction factor

Calibration mix No.	Calculated	Observed	Correction factor
16-146	0.010137	0.010175	0.996265
		0.010170	0.996755
		0.010170	0.996755
16-147	0.010334	0.010365	0.997009
		0.010364	0.997105
		0.010364	0.997105
		Average =	0.99683

Absolute ratio

Observed	Corrected
0.0101698	0.010138
0.0101701	0.010138
0.0101777	0.010145
0.0101727	0.010140
0.0101690	0.010137
0.0101728	0.010141
Average =	0.010140

Table 23. Absolute $^{235}U/^{238}U$ ratio of SRM U-005.

Calculation of correction factor

Calibration mix No.	Calculated	Observed	Correction factor[a]
16-148	0.0048020	0.0048110	0.998129
		0.0048130	0.997715
		0.0048073	0.998898
		0.0048075	0.998856
16-149	0.0050110	0.0050219	0.997830
		0.0050185	0.998506
		0.0050181	0.998585
		0.0050165	0.998904
		Average =	0.99843

Absolute ratio

Observed	Corrected
0.0049273	0.0049195
0.0049245	0.0049167
0.0049313	0.0049235
0.0049225	0.0049147
0.0049275	0.0049197
0.0049270	0.0049192
0.0049233	0.0049155
0.0049235	0.0049157
Average =	0.004918

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[a] The standard high temperature procedure was used for this SRM.

10. Isotopic Analysis of Calibration Mixes and SRM U-970

SRM U-970 was the most enriched of the uranium SRMs and was the largest $^{235}U/^{238}U$ ratio to be determined by the point calibration technique. The 12-inch radius of curvature 68° analyzer tube mass spectrometer with a "Z" lens source and a tube beam valve was used. A modified low temperature procedure was used and the total ion current intensity was approximately $4\text{-}5\times10^{-11}$A and growing. The four calibration mixes were analyzed in an alternate pattern with two different solutions of SRM U-970 until duplicate analyses were obtained for each mix and a total of 4 analyses for each SRM solution. Table 24 summarizes the calculation of correction factors and the absolute $^{235}U/^{238}U$ ratio.

Table 24. Absolute $^{235}U/^{238}U$ ratio of SRM U-970.

Calculation of correction factors

Calibration mix No.	Calculated	Observed	Correction factor[a]
17-86	193.785	194.791	0.994835
		194.826	0.994656
17-92	190.956	191.972	0.994707
		191.878	0.995194
17-93	197.106	198.327	0.993843
		198.116	0.994901
17-94	191.316	192.400	0.994365
		192.283	0.994970
		Average =	0.99468

Absolute ratio

Observed	Corrected
187.679	186.680
187.738	186.739
187.716	186.717
187.687	186.688
187.874	186.874
187.942	186.942
187.763	186.764
187.847	186.848
Average =	186.78

---

[a] The standard low temperature procedure was used for this SRM.

7. ABSOLUTE ISOTOPIC ABUNDANCE BY ^{233}U ISOTOPE DILUTION

A. Introduction

The initial method of measuring uranium isotopic composition was to mass scan (magnet) all isotopes at a constant rate; select adequate decade sensitivity to give a maximum deflection for each peak; then calculate the isotopic composition over a small number of peak sets (∿10). The chief disadvantage of this method was the relatively large amount of time spent on baselines that were constant between the major isotopes and the relatively small amount of time on peak tops that were continuously changing in magnitude. An alternate method was developed to take advantage of the constant baselines of the major isotopes and consisted of the following steps: measure the ^{235}U/^{238}U ratio at the beginning and end of the data period of each analysis by the "peak hopping" technique; compare the minor isotopes with respect to ^{235}U as a reference peak; calculate isotopic abundance ratios and then the isotopic composition. This method provided superior ^{235}U/^{238}U measurements without compromising the precision of baseline determinations. A constant rate of scanning was still essential for minor isotope measurements in order to accurately determine baselines of the smaller peaks on the tail of ^{235}U.

The improved measurement technique and exclusive use of the expanded scale recorder reduced the limit of error below 0.5 percent for most minor isotope measurements. Further modifications were made to give better vacuums which produced a significant reduction in the scatter from the ^{235}U peak, but the precision of the minor isotope measurements was larger than could be accounted for under the analytical conditions of the experiment. Since the ratio of the ^{235}U with respect to the minor isotopes was always between 50 and 660, it was concluded that much of the imprecision was simply inability to measure such large ion current ratios without non-linear effects increasing the scatter of the data.

Thus, the ^{233}U isotope dilution technique was utilized to circumvent the requirement of measuring large ion current ratios to determine minor isotope composition. The ^{233}U spike was added to each SRM to approximate the ^{234}U abundance and, exclusive of SRM U-0002, the entire series of measurements was reduced to comparing ion current ratios that were less than twelve.

For SRM U-0002, the ^{238}U isotope comprised 99.98 atom percent of the sample and only two other isotopes were detected above the 1 ppm level. A precise and accurate comparison of such a large ion current ratio was not practical, so isotope dilution was used to evaluate the ^{234}U and ^{235}U abundances of this SRM.

B. Experimental Procedure

1. Mass Spectrometry

Isotopic measurement of the spiked SRMs and the calibration standards were made on the single-stage solid sample mass spectrometer briefly described in Section 6,B,1. The only significant change in instrumentation was the use of an ion multiplier for SRMs with isotopic abundance less than 0.1 atom percent. After the "Z" lens source became a part of the standard instrumentation, minor isotope measurements for all but four of these SRMs were reevaluated.

Exclusive of SRM U-0002 and SRM U-970, an unspiked solution and at least one spiked solution were analyzed for each SRM. A single analysis of the unspiked solution was made first and was then followed by three analyses of the spiked solution. The ratio measurement consisted of measuring ^{234}U and ^{236}U with respect to ^{235}U for the unspiked solutions and also ^{234}U and ^{236}U with respect to ^{233}U for the spiked solutions. Magnet scanning was at a constant rate with a quick scan step (∿2 seconds) used for the ^{235}U peak of the spiked samples. Each analysis was started and concluded with a ^{235}U/^{238}U ratio measurement.

A high temperature analytical procedure or a modification of this technique was used for all SRMs except SRM U-970. Corrections for the effects of bias were determined by analyzing SRM U-500 under the same experimental conditions as the spiked samples or by using the $^{235}U/^{238}U$ ratio of the spiked SRM as a known to make an internal normalization for filament bias effects.

2. Isotopic Analysis of "U233" Separated Isotope, Lot No. 3

The 12-inch radius of curvature 68° analyzer tube mass spectrometer was equipped with an ion multiplier. When this series of measurements was made, the most accurate isotopic standard available with ion current ratios similar to "U233" was a Belgian Congo natural uranium sample with the $^{235}U/^{238}U$ ratio determined by uranium hexafluoride mass spectrometry [20]. The Belgian Congo sample was used as a calibration standard and was analyzed under the same conditions to determine correction factors. The isotopic composition calculated from corrected ratios is given in Table 25. The ^{236}U isotope was not detected and was believed to be less than 1 ppm.

Table 25. Isotopic composition of "U233" separated isotope, Lot No. 3.

Isotope	Atom percent
^{233}U	99.924 ±0.002[a]
^{234}U	0.0180 ±0.0004
^{235}U	0.0012 ±0.0004
^{238}U	0.0566 ±0.0006

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[a] The uncertainties are 95% C.L.

3. Preparation of Spiked SRMs U-005 through U-930

a. Procedure - Each sample was ignited (Section 6,B,3) and then the platinum boat and sample were carefully transferred to a teflon bottle (0.5 g samples to 125 ml bottles and 1 g samples to 250 ml bottles) which had been wrapped in a damp paper towel. Sufficient nitric acid (1+1) was added to the bottle to give a solution of nitric acid (1+19) containing 5 mg U per ml when the "U233" spike and water had been added. The bottle was sealed with a teflon lined cap and heated on a steam bath for an additional 1/2 hour after all the sample had appeared to dissolve. The "U233" separated isotope samples were dissolved after the 16 isotopic standards had been dissolved. After dissolution, the "U233" sample was diluted to an equivalent of approximately 1 mg of U_3O_8/ml of solution.

The cap on the "U233" bottle was replaced with a similar cap that had inserted in it a piece of polyethylene tubing shaped for use as a "squirt" bottle. The outside end of the tubing was sealed with a polyethylene cap to prevent evaporation. The next more dilute solution of the "U233" was prepared before the samples were spiked. The polyethylene tube sealer was removed and a small quantity of solution was squirted into a waste bottle. The sealer was quickly replaced, the bottle was allowed to stand 2-3 mminutes and then wiped with a damp paper towel. After standing 1/2 minute the bottle was weighed to the nearest 0.1 mg on a 200 g capacity magnetically damped balance. An empty 125 ml teflon bottle was wiped with a damp towel, allowed to stand 1/2 minute and weighed. The sealer was removed from the "U233" spike bottle and the calculated amount of solution was squirted into the uncapped empty bottle. Both bottles were reweighed after quickly resealing and wiping as before. Sufficient nitric acid (1+19) was added to the bottle containing the next dilution, to dilute it to the required concentration of ^{233}U. The amount of spike added was calculated from the weight change of the "U233" spike bottle and the aliquot receiving bottle, being open and subject to evaporation loss, was used as an approximate check.

The SRM samples were spiked as above except the final dilution was with water to give a nitric acid (1+19) solution containing 5 mg U/ml.

b. Discussion of Procedure - These were the first uranium SRM samples to have the "U233" spike added by weight aliquoting. The amount of "U233" separated isotope needed to nearly equal the ^{234}U isotopic content of each sample was calculated. The ^{234}U content of the samples varied over a large range, 0.002 percent to over 1 percent. This meant that for practical size samples several concentrations of "U233" separated isotope solution would be required. It was decided to use 0.5 and 1.0 g samples of the SRMs with additional SRM samples "spiked" at each change in dilution of the "U233" solution to provide a check on the dilution accuracy. Two "U233" separated isotope samples were used for duplication to ensure reliability of the results.

Approximately 0.1 g samples of "U233" separated isotope were used and diluted to approximately 100 g of solution after dissolving in nitric acid (1+1).

The sample bottles receiving the "U233" solutions were weighed before and after receiving their aliquot to give a check on the amount of aliquot added. These bottles were open while receiving the aliquot and lost weight caused by evaporation but they did insure that weight recording errors or possible loss by splattering did not exceed a few milligrams. The difference in weight of aliquot calculated from the spike bottle and the receiving bottle was 2 to 7 mg.

The moles of "U233" added were calculated using equation {3} and the moles of SRM calculated using equation {2}. The aliquoting data is given in Tables 26 and 27.

Table 26. Composition of "U233" spiked solutions of SRM U-930 through SRM U-005, series A.

"U233" solution No.	Aliquot (g soln)	Isotopic standard Weight (g U_3O_8)	SRM
1A[a]	10.9640	1.005215	U-930
"	7.8411	0.998426	U-900
"	6.3595	1.006923	U-850
"	6.6203	1.003400	U-800
"	6.0516	1.037086	U-750
"	5.2925	1.017446	U-500
2A[b]	12.9181	0.506272	U-500
"	12.5021	0.999547	U-350
"	6.0825	0.997625	U-200
"	4.9750	1.004893	U-150
"	3.3367	1.022924	U-100
3A[c]	12.1196	0.453468	U-100
"	11.1938	0.996259	U-050
"	7.4311	0.997973	U-030
"	4.9790	1.009391	U-020
4A[d]	12.5783	0.515267	U-020
"	8.8460	0.517468	U-015
"	9.5006	0.880029	U-010
"	5.2036	1.177292	U-005

---

[a] 3.6134 micromoles U/g of solution.

[b] 0.72232 micromoles U/g of solution.

[c] 0.089989 micromoles U/g of solution.

[d] 0.017973 micromoles U/g of solution.

Table 27. Composition of "U233" spiked solutions of SRM U-930 through SRM U-005, series B.

"U233" solution No.	Aliquot (g soln)	Isotopic standard	
		Weight (g U_3O_8)	SRM
1B[a]	10.8180	1.006699	U-930
"	7.7439	1.002125	U-900
"	6.6193	1.019177	U-850
"	6.5364	1.004216	U-800
"	6.0349	1.010581	U-750
"	5.2043	1.018733	U-500
2B[b]	13.5146	0.508439	U-500
"	12.7793	1.037252	U-350
"	6.3829	1.013953	U-200
"	4.9651	1.015415	U-150
"	3.5400	1.054223	U-100
3B[c]	12.2564	0.463396	U-100
"	11.1232	0.997781	U-050
"	7.6342	0.995414	U-030
"	4.9636	1.009075	U-020
4B[d]	12.6011	0.502228	U-020
"	8.4375	0.499685	U-015
"	9.9743	0.897315	U-010
"	5.1542	1.177409	U-005

---

[a] 3.5906 micromoles U/g of solution.

[b] 0.71587 micromoles U/g of solution.

[c] 0.089050 micromoles U/g of solution.

[d] 0.017800 micromoles U/g of solution.

4. Preparation of Spiked SRMs U-0002 and U-970

a. Procedure - The samples were ignited (Section 6,B,3) transferred to teflon bottles and dissolved as before (Section 6,B,4). The "U233" separated isotope samples were diluted to approximately 1 mg of U/ml of solution for the SRM U-970 samples and aliquots of these "U233" solutions were diluted to approximately 40 μg of U/ml of solution for the SRM U-0002 samples. The "U233" solution aliquots were weighed using a 5 ml plastic syringe as before (Section 6,B,5). The spiked solutions were mixed, diluted with water to give 5 mg U/ml and mixed again.

b. Discussion of Procedure - The analysis of these two SRM samples was started after the first 16 uranium isotopic standards were completed. Although these two samples of widely different isotopic composition were determined at the same time, all operations in the handling of them were done separately, with care taken to insure that the chance of any cross contamination was minimized.

Six samples of SRM U-970 were spiked with two different "U233" solutions. On three of the samples ^{233}U was added to approximately equal the ^{234}U content of the SRM U-970 and on the other three, ^{233}U was added to approximately equal the ^{238}U content.

Six samples of SRM U-0002 were spiked with the more dilute "U233" solutions, approximately 40 μg U/ml of solution. Four samples were spiked to equal the ^{235}U content. The other two samples of SRM U-0002 were spiked with enough ^{233}U to equal approximately ten times the ^{234}U content.

The first results on SRM U-970 samples indicated approximately 0.4 percent difference between samples spiked with "U233" solution number 1 and those spiked with "U233" solution 2. Direct mass spectrometer determinations on SRM U-970 solutions agreed to within experimental error with samples spiked with "U233" solution 1. This indicated that solution 2 probably

Table 28. Spike calibration of "U233" separated isotope solutions.

"U233" soln No.	"U235" soln No.	"U233" (g soln)	"U235" (g soln)	Ratio $^{233}U/^{235}U$	Micromole ^{233}U/g of solution	
					Experimental	Calculated
1	1[a]	4.34538	2.47621	1.0493	4.0948	
1	2[b]	4.23364	2.52287	1.0037	4.0960	
1	1	4.30217	2.41923	1.0606	4.0974	
				Average =	4.0961	4.0981
				s.d. =	0.0013	
2	2	4.38503	2.49916	1.0397	4.0579	
2	1	4.28589	2.41252	1.0490	4.0567	
2	2	4.23708	2.43332	1.0290	4.0599	
				Average =	4.0582	4.0792
				s.d. =	0.0016	

---

[a] 6.8488 micromoles ^{235}U/g solution.

[b] 6.8707 micromoles ^{235}U/g solution.

did not contain as much ^{233}U as calculated from the weight of oxide. The ^{233}U content of both solutions was determined by isotope dilution using two "U235" separated isotope solutions (Table 28). The concentration of ^{233}U in "U233" solution 1 as determined by isotope dilution mass spectrometry agreed to within 0.05 percent of the concentration calculated by using the weight of oxide. The concentration of ^{233}U in "U233" solution 2 was 0.51 percent less than that calculated from the weight of oxide. The reason for the low value was not ascertained. Three possibilities suggest themselves: an impure or contaminated "U233" sample, loss of U_3O_8 sample, or an incorrect weight recorded. Any of these possibilities could account for the difference but there is no way of determining which one.

The corrected "U233" spike addition to SRMs U-970 and U-0002 are given in Tables 29 and 30.

Table 29. Composition of "U233" spiked solutions of SRM U-970.

	"U233"		U-970
Sample No.	Soln No.	g of soln	g of U_3O_8
17-76	1[a]	3.18399	0.675190
17-77	2[b]	3.00664	0.657376
17-78	1	2.95284	0.651655
17-83	2	4.67254	0.323509
17-84	1	4.76840	0.323215
17-85	2	4.81086	0.328024

---

[a] 4.0961 micromoles ^{233}U/g solution.

[b] 4.0582 micromoles ^{233}U/g solution.

Table 30. Composition of "U233" spiked solutions of SRM U-0002.

	"U233"		U-0002
Sample No.	Soln No.	g of soln	g of U_3O_8
17-68	1-2[a]	0.36219	1.250375
17-69	1-2	4.79468	1.206183
17-70	2-2[b]	0.62141	1.513389
17-71	2-2	4.43024	1.135712
17-72	2-2	4.72277	1.201320
17-73	1-2	4.63259	1.211331

---

[a] 0.163531 micromoles ^{233}U/g solution.

[b] 0.161327 micromoles ^{233}U/g solution.

5. Analysis of SRMs U-005 through U-150 to Determine Minor Isotope Composition with Ion Multiplier Detection

Minor isotope compositions were determined in two steps by using ion multiplier detection for abundances less than 0.1 atom percent and then by using the standard NBS collector for abundances greater than 0.1 atom percent. An abundance of 0.1 atom percent was the crossover point at which both methods were to be used. The source was the standard linear thin lens without the "Z" focussing plates. A modified high temperature procedure with a total intensity of approximately 8×10^{-11}A was used and the intensity was further reduced when the ^{235}U abundance was large enough to saturate the VRE.

The corrections for bias were made by analyzing SRM U-500 under the same experimental conditions as all other samples. Because of the gross difference in isotopic composition, SRM U-500 was usually analyzed on a clean source, but a small number of samples were analyzed on the same source as the spiked SRMs just prior to removal of the source for cleaning.

There was no significant experimental difference between the two groups of data and it was added support for the conclusion that uranium memory was not normally detectable over a large isotopic composition range. SRM U-200 was analyzed to provide a minimum of 3 points for comparison of multiplier and standard collector data and is not the preferred method for this minor isotope abundance. The correction factors were determined to be 1.0040 and 1.0120 for the $^{234}U/^{233}U$ and $^{236}U/^{233}U$ ratios, respectively. Composition of the minor isotopes was calculated using equation {4} and is summarized in Table 31.

$$\text{Isotopic Composition} = R_c \left[\frac{m_s}{m_{SRM}} - \frac{m_i}{m_{SRM}} \right] 100 \qquad \{4\}$$

R_c = Ratio of minor isotope with respect to ^{233}U corrected for bias

m_s = micromoles of spike

m_{SRM} = micromoles of SRM sample

m_i = micromoles of minor isotope in "U233" spike

6. Analysis of SRMs U-100 through U-930 to Determine Minor Isotope Composition

The source was the standard thin lens without "Z" focussing plates. A high temperature analytical procedure was used and the total U^+ ion current was approximately 1×10^{-10}A. The standard practice of analyzing uranium in groups of samples covering approximately 20 percent in ^{235}U isotopic composition, and cleaning the source prior to analyzing each group was used to further minimize the chance of significant memory. Since the $^{235}U/^{238}U$ ratio of each SRM was known from previous measurement, corrections for bias were determined internally for each analysis by calculating the ratio of the theoretical

Table 31. Minor isotope composition of SRM U-005 through SRM U-200 using ion multiplier detection.

SRM	Sample No.	^{233}U added[a]	Observed ratios $^{234}U/^{233}U$	$^{236}U/^{233}U$	Atom percent ^{234}U	^{236}U
U-005	13-51	0.0002228	0.97565	2.0660	0.00218	0.00466
U-010	13-57	0.005442	0.99110	1.2375	0.00541	0.00682
U-015	13-70	0.008617	0.98277	1.8798	0.00850	0.01639
U-020	13-77	0.012304	1.01137	1.32567	0.01249	0.01651
U-020	13-80	0.012448	0.99869	1.31041	0.01248	0.01651
U-030	13-83	0.018789	1.00764	1.07142	0.01901	0.02038
U-050	13-86	0.028347	0.98168	1.67269	0.02794	0.04799
U-100	13-95	0.067387	0.99967	0.55233	0.06762	0.03767
U-100	13-98	0.067406	1.01970	0.56552	0.06758	0.03779
U-150	13-104	0.100142	0.98786	0.65054	0.09931	0.06594
U-200	13-109	0.123265	1.00974	1.70058	0.12495	0.21216

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[a] Atom percent.

$^{235}U/^{238}U$ to the observed $^{235}U/^{238}U$. The data is given in Table 32 for the average of 3 analyses per solution.

7. Re-evaluation of Minor Isotope Composition of SRMs U-030 through U-500 Using the "Z" Source

Subsequent to completion of the intial minor isotope determinations by ^{233}U dilution, the "Z" lens source was developed and became part of the standard instrumentation. Since it was possible to achieve greater ion current intensities and maintain the high degree of control necessary to accurately correct for fractionation effects, a third series of measurements was undertaken to demonstrate an extension of the lower limit for precise minor isotope measurements and to increase the number of SRMs with isotope measurements using conventional detection. A high temperature analytical procedure was used and the total U^+ ion current ranged from approximately 3×10^{-10}A for SRM U-500 to 5×10^{-10}A for SRM U-030. Other than increased signal intensity there were no major changes in the analytical method. Data is given in Table 33 for the average of three analyses per solution.

8. Analysis of SRM U-970 to Determine Minor Isotope Composition

Two groups of three spiked SRM samples were prepared with the ^{233}U approximating either the ^{234}U or the ^{238}U composition. The three-fold purpose of the equal atom ^{238}U group was to cross check ^{238}U by isotope dilution; to provide a spike within a factor of 3 of the ^{236}U composition; and to obtain measurements on a $^{234}U/^{233}U$ ratio other than 1.

A low temperature procedure for the "Z" source was used and the total U^+ ion current was $5\text{-}7\times10^{-11}$A. Larger ion currents were not used because it could not be satisfactorily demonstrated that the measuring circuit recovered completely from the effects of R-C response in switching from a 10^{-10}A to a 10^{-13}A ion current. For this type of measurement, failure to recover was not correctable on the basis of a point calibration and would result in a systematic enhancement of

Table 32. Minor isotope composition of SRM U-100 through SRM U-930 using the NBS collector.

SRM	Sample No.	^{233}U added[a]	Observed ratios $^{234}U/^{233}U$	$^{236}U/^{233}U$	Corr factor (3 mass unit)	Atom percent ^{234}U	^{236}U
U-100	13-97	0.066043	1.02300	0.571387	1.0027	0.06761	0.03784
U-100	13-98	0.067406	1.00185	0.561220	1.0027	0.06758	0.03793
U-150	13-105	0.098101	1.01198	0.671400	1.0035	0.09938	0.06610
U-200	13-108	0.126227	0.98565	1.67457	1.0025	0.12449	0.21190
U-350	13-112	0.246638	1.01096	0.676869	1.0019	0.24945	0.16726
U-500	13-119	0.531270	0.97456	0.141599	1.0024	0.51807	0.07541
U-500	13-121	0.512125	1.01097	0.146838	1.0024	0.51806	0.07538
U-750	13-124	0.596991	0.99184	0.418104	1.0021	0.59242	0.25013
U-800	13-129	0.650327	1.00839	0.375144	1.0021	0.65613	0.24447
U-850	13-134	0.648592	0.99190	0.569944	1.0014	0.64355	0.37018
U-900	13-135	0.771247	1.00726	0.429802	1.0030	0.77748	0.33248
U-930	13-143	1.07212	1.00875	0.188750	1.0015	1.08185	0.20267

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[a] Atom percent.

Table 33. Redetermination of minor isotope composition of SRM U-030 through SRM U-500 using the NBS collector and the "Z" lens source.

SRM	Sample No.	^{233}U added[a]	Observed ratios $^{234}U/^{233}U$	Observed ratios $^{236}U/^{233}U$	Corr factor (3 mass unit)	Atom percent ^{234}U	Atom percent ^{236}U
U-030	13-83	0.018789	1.00929	1.08549	1.0002	0.01896	0.02039
U-030	13-84	0.019166	0.990221	1.06554	1.0002	0.01898	0.02042
U-050	13-85	0.027852	0.999862	1.72497	1.0007	0.02785	0.04808
U-050	13-86	0.028347	0.981798	1.69306	1.0007	0.02784	0.04803
U-100	13-95	0.067387	1.00339	0.561520	1.0016	0.06765	0.03790
U-100	13-97	0.066043	1.02354	0.572829	1.0016	0.06763	0.03789
U-100	13-98	0.067406	1.00350	0.561821	1.0016	0.06768	0.03793
U-100	13-99	0.066020	1.02410	0.573994	1.0016	0.06764	0.03796
U-150	13-104	0.100142	0.991452	0.657252	1.0016	0.09932	0.06592
U-150	13-105	0.098101	1.01287	0.671897	1.0016	0.09940	0.06602
U-200	13-108	0.126227	0.987090	1.67269	1.0023	0.12466	0.21162
U-200	13-109	0.123265	1.01030	1.71212	1.0023	0.12460	0.21153
U-350	13-110	0.252463	0.988885	0.661574	1.0019	0.24976	0.16734
U-350	13-112	0.246638	1.01277	0.677215	1.0019	0.24989	0.16734
U-500	13-118	0.514201	1.00726	0.146488	1.0019	0.51815	0.07547
U-500	13-119	0.531270	0.974322	0.141849	1.0019	0.51785	0.07550
U-500	13-120	0.524395	0.987973	0.143971	1.0019	0.51831	0.07564
U-500	13-121	0.512125	1.01121	0.147274	1.0019	0.51808	0.07557

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[a] Atom percent.

the ^{234}U and ^{236}U peaks. Each set of equal atom samples were analyzed as a group. Within the equal atom ^{234}U group triplicate analyses were made for all spiked samples and, for the equal atom ^{238}U group, duplicate analyses were made for each sample.

The minor isotopes were compared by the normal magnet scanning procedure and at all times the ^{235}U/^{238}U and ^{238}U/^{233}U ratios were measured by alternating between peak tops. The ^{235}U/^{238}U ratio was used strictly as an indicator of the position on the fractionation curve for each analysis, and the correction for bias effects was determined by analyzing SRM U-500 on a cleaned source and under the same experimental conditions as the spiked samples. The correction factors for ^{234}U/^{233}U, ^{236}U/^{233}U and ^{238}U/^{233}U were found to be 1.0014, 1.0042 and 1.0070 respectively. The calculation of isotopic composition is summarized in Tables 34 and 35.

9. Analysis of SRM U-0002 to Determine ^{235}U by Isotope Dilution

A high temperature procedure for the "Z" lens source was used and the total U^+ ion current was $4\text{-}5\times10^{-10}$A. The tube beam valve was part of the standard instrumentation and it was possible to operate with higher collector vacuums than were previously obtainable. For this particular isotopic distribution and signal intensity it was demonstrated that the collector vacuum was normally too high and scattered particles rendered baselines at the ^{235}U and ^{236}U mass positions indeterminate. With respect to the ^{238}U ion current of $4\text{-}5\times10^{-10}$A the interference was less than one part in 100,000 but was approximately 2-5 percent of the ^{233}U and ^{235}U peak heights.

The continuous baseline curve was obtained with an estimated collector pressure of $1\text{-}4\times10^{-7}$ torr. At an estimated pressure of 4×10^{-7} torr, the scatter tail from the large ^{238}U peak was significant. As the pressure was reduced below 1×10^{-7} torr and approached mid-range 10^{-8} torr, interference from scattered secondary particles was significant. An optimum

Table 34. Minor isotope composition of SRM U-970.

Sample No.	^{233}U added[a]	Observed ratios ^{234}U/^{233}U	Observed ratios ^{236}U/^{233}U	Atom percent ^{234}U	Atom percent ^{236}U
17-76	0.53642	3.10020	0.276844	1.66524	0.14912
		3.10089	0.277498	1.66561	0.14948
17-77	0.51545	3.22932	0.288310	1.66679	0.14923
		3.22489	0.287253	1.66450	0.14868
17-78	0.51545	3.22820	0.287926	1.66621	0.14903
		3.22743	0.287446	1.66581	0.14878
17-83	1.62776	1.02054	0.091398	1.66322	0.14939
		1.02133	0.091314	1.66451	0.14926
		1.02147	0.091141	1.66474	0.14897
17-84	1.67819	0.991292	0.088597	1.66560	0.14930
		0.991055	0.088484	1.66520	0.14911
		0.991412	0.088496	1.66580	0.14913
17-85	1.65287	1.00586	0.089960	1.66458	0.14931
		1.00621	0.089773	1.66516	0.14900
		1.00614	0.089848	1.66504	0.14913
			Average =	1.6652	0.1491

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[a] Atom percent.

Table 35. ^{238}U in SRM U-970 by isotope dilution.

Sample No.	^{233}U added[a]	Observed $^{238}U/^{233}U$	Atom percent ^{238}U
17-76	0.53642	0.969450	0.52336
		0.969326	0.52330
17-77	0.51545	1.00884	0.52335
		1.00782	0.52282
17-78	0.51545	1.00725	0.52252
		1.00715	0.52249
17-83	1.62776	0.319206	0.52230
		0.319655	0.52304
		0.319588	0.52293
17-84	1.67819	0.309926	0.52280
		0.310564	0.52383
		0.310254	0.52335
17-85	1.65287	0.314909	0.52321
		0.314910	0.52321
		0.314968	0.52330
		Average =	0.5230

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[a] Atom percent.

pressure of approximately 2×10^{-7} torr gave a spectrum with no baseline interference and a relatively small scatter contribution from the ^{238}U peak but this pressure could not be maintained long enough to complete the ratio measurement. Thus, the objective of the modified procedure used for this measurement was to raise the base pressure of the collector from 10^{-9} torr and maintain it between limits ($<3\times10^{-7}>8\times10^{-8}$) that would avoid significant scatter contributions from the tail of the ^{238}U peak or baseline interference by secondary particles. To acheive this goal it was necessary to condense the pumpdown time and to abandon the normal procedure of sample degassing, and to reduce the long waiting period proceeding the analysis. The normal pumping time for a uranium analysis was modified as follows: allow 5 minutes of source pumping by the mercury diffusion pump; open the tube beam valve for an additional ten minutes of pumping; add liquid nitrogen to the source coldfinger and start the degassing procedure. Immediately after completing the normal 15 minute sample degassing, the ion accelerating voltage was increased to 10 kV and the sample was degassed at higher temperatures for another 15 minutes. At the beginning of the high temperature degassing the U^+ signal intensity was adjusted to 1.3×10^{-10}A and was increased by this increment every 5 minutes until the total intensity was approximately 4×10^{-10}A. After a combined total of 30 minutes of degassing, the filaments were turned OFF, the beam valve was closed and the source coldfinger warmed to room temperature. After a five minute waiting period the analysis was restarted and a 4×10^{-10}A ion current was obtained in the prescribed manner for a high temperature analysis during the next 20 minutes.

Approximately one hour after the start of pumping the ratio measurement was started with an estimated collector pressure of $1\text{-}2\times10^{-7}$ torr. Extensive pumping either before or after degassing, even with the beam valve open, was detrimental because the collector vacuum became too high before the analysis could be completed. Completing the analysis within 2 hours after the start of pumping on the sample was mandatory in order to avoid detectable interference at the baselines.

The correction for bias was determined by analyzing SRM U-500 on a cleaned source and under the same experimental conditions as the spiked samples. The correction factor for the $^{235}U/^{233}U$ ratio was found to be 1.0014. The ^{235}U in SRM U-0002 is given in Table 36. Because of the small probability of some organic contribution at an ionizing filament temperature of 2160 °C, a single analysis of most spiked samples was made on the two-stage mass spectrometer using pulse counting techniques. The measurements were made at a lower ionizing filament temperature and under conditions of zero detectable organic background. These results are given in Table 37 for comparison with the conventional detector data.

Table 36. ^{235}U in SRM U-0002 by isotope dilution.

Sample No.	^{233}U added[a]	Observed $^{235}U/^{233}U$	Atom percent ^{235}U
17-69	0.018248	0.959330	0.017530
		0.960011	0.017542
		0.961432	0.017568
17-71	0.017666	0.984336	0.017549
		0.983385	0.017532
		0.985569	0.017571
17-73	0.017556	0.999208	0.017567
		0.996700	0.017522
		0.997662	0.017539
		Average =	0.01755

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[a] Atom percent.

Table 37. ^{234}U and ^{235}U in SRM U-0002 by pulse counting.

		Atom percent	
Sample No.	^{233}U added[a]	^{234}U	^{235}U
17-68	0.001330	0.000164	
17-70	0.001859	0.000162	
17-69	0.018248	0.000157	0.01759
17-71	0.017666	0.000158	0.01762
17-72	0.017804	0.000158	0.01749
17-73	0.017556		0.01758
	Average =	0.00016	0.01757

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[a] Atom percent.

10. Analysis of SRM U-0002 to Determine ^{234}U by Pulse Counting

Because of low isotopic composition, pulse counting was the method of determining the ^{234}U content of SRM U-0002. These measurements were made by L. J. Moore of the Analytical Mass Spectrometry Section on the two stage mass spectrometer. A description of the procedure is given below.

The same set of SRM U-0002 samples, which were spiked with the "U233" solution and used for determination of the ^{235}U content, also presented an opportunity to determine the ^{234}U content, which was known to be <2 ppm. To provide a statistically useable ^{234}U signal of ∿100 counts per second, an equivalent ^{238}U signal of approximately 50 million counts was required. The single V filament technique used for the 0.02 ppm trace elements in glass series [8] proved to be inadequate in terms of total signal intensity available. Therefore, a fourfold modification of the conventional triple filament technique was used:

(1) Ionizing and sample filaments were degassed at ∿2050 °C for one hour.

(2) One-half the usual amount of uranium was used; i.e., approximately 50 μg per sample filament.

(3) A 30 minute degassing period was used prior to analysis, with the ionizing filament set at 2150 °C and the sample filament currents set at 1.75 A.

(4) An ionizing filament temperature of 1900 °C was used during analysis to eliminate the contribution of organic ions to the uranium spectrum.

A final ^{238}U signal of ∿1.6 V on a 10^{11} ohm input resistor to the VRE gave the requisite 100 cps ^{234}U signal.

A scan of the mass region from mass 237 through 233 during an analysis of SRM U-0002 spiked with "U233" solution showed there was no discernible organic or other contribution to mass position 236, nor in a scan of unspiked SRM U-0002 was there any evidence of a contribution at the 236 or 233 mass positions. Therefore, the only correction required for any contribution to the various mass positions above the normal background was for the scatter due to the tail of the large ^{238}U beam. To determine the magnitude of the correction, a count was taken, immediately prior to analysis, for 100 seconds at the half-mass positions on either side of each integral mass position of interest. An average of the two half-mass counting results then represented an approximate scatter correction for the corresponding integral mass position. Since the scatter correction for the ^{234}U amounted to ∿5 percent of the total count, the accuracy of the analysis was limited largely by the inability to accurately correct for scatter.

A mass discrimination correction was applied by also measuring the ^{233}U/^{235}U ratio and comparing the corresponding ratio as determined by the conventional triple filament technique. The ^{234}U data for the pulse counting measurements is given in Table 37.

C. Results and Discussion

The NBS determined values for $^{235}U/^{238}U$ ratios and the minor isotopic composition by ^{233}U dilution are given in Table 38. This data was used to calculate the isotopic composition of the least abundant of the ^{235}U and ^{238}U isotopes, and composition of the remaining isotope was determined by difference.

Table 38. Summary of NBS determined $^{235}U/^{238}U$ ratios and the isotope dilution values of ^{234}U and ^{236}U for SRMs U-0002 through U-970.

SRM	$^{235}U/^{238}U$ Ratio	^{234}U[a]	^{236}U[a]
U-0002		0.00016	<0.00001
U-005	0.004918	0.00218	0.00466
U-010	0.010140	0.00541	0.00681
U-015	0.015566	0.00850	0.01639
U-020	0.02081	0.01248	0.01651
U-030	0.03143	0.01897	0.02041
U-050	0.05278	0.02787	0.04804
U-100	0.11360	0.06761	0.03790
U-150	0.18108	0.09934	0.06601
U-200	0.25119	0.12459	0.21168
U-350	0.5464	0.24970	0.16730
U-500	0.9997	0.51808	0.07547
U-750	3.164	0.59243	0.25014
U-800	4.268	0.65614	0.24448
U-850	6.148	0.64352	0.37015
U-900	10.375	0.77751	0.33246
U-930	17.356	1.08183	0.20265
U-970	186.78	1.66520	0.14912

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[a] Atom percent.

The ^{235}U values of SRMs U-005 through U-350 and the ^{238}U values of SRMs U-750 through U-930 were converted to weight percent composition and are given in Table 39 with measurements by Union Carbide Nuclear Company (UCNC), Oak Ridge, Tennessee, and by Goodyear Atomic Corporation (GAT), Portsmouth, Ohio.

Table 39. Comparison of ^{235}U and ^{238}U measurement by NBS, UCNC and GAT.

		Weight percent ^{235}U	
SRM	NBS	UCNC[a]	GAT[a]
U-005	0.4832	0.4834	0.4834
U-010	0.9911	0.9911	0.9915
U-015	1.513	1.513	1.513
U-020	2.013	2.013	2.013
U-030	3.009	3.009	3.008
U-050	4.949	4.948	4.950
U-100	10.075	10.078	10.077
U-150	15.143	15.139	15.146
U-200	19.807	19.812	19.811
U-350	34.899	34.906	34.904
		Weight percent ^{238}U	
U-750	24.045	24.032	24.030
U-800	19.007	19.018	19.014
U-850	14.006	13.997	14.002
U-900	8.795	8.795	8.796
U-930	5.443	5.445	5.445

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[a] The only isotope determined in the SRM was the least abundant of the two major isotopes.

The UCNC and GAT measurements were made by uranium hexafluoride anlaysis in which each SRM was compared to a set of bracketing synthetic calibration mixes prepared from oxide blends of enriched and depleted uranium. Separation of NBS data into a point calibration group and an interpolation group for comparison with values by UCNC and GAT does not reveal any significant systematic differences. The magnitude of the deviations for the interpolation data is, as might be expected, slightly larger than that for the point calibration group. The only SRM with a ratio determination by both techniques at NBS is U-050 and the agreement is well within experimental error.

The consistency of the NBS interpolation data with respect to the independent measurements by GAT and UCNC provided the foundation for evolution of the method into the systems calibration technique. The systems calibration is designed to test the linearity of the measuring circuit over a wide range of isotopic ratios by evaluating the consistency of the filament bias under identical experimental conditions for all samples. If the bias is constant, within experimental error, for each ratio over the range tested, a single correction factor is valid for all isotopic ratios within that range. SRMs U-930 through U-050 is the group of standards used for this measurement and all of the $^{235}U/^{238}U$ ratios are within the limits 20 to 0.05. The measurement of ion current ratios outside of this range is subject to errors due to non-linearity of the measuring circuit and all such ratios must be corrected using the point calibration technique. The systems calibration is a very sensitive and rigorous test for defining the linear response range of the measuring circuit and is recommended for each new or rebuilt mass spectrometer. Finally, the systems calibration is useable as an exacting performance test for the operator who is learning how to apply the rules of a fixed analytical procedure and is a recommended means of evaluating operator performance. The body of data accumulated from systems calibration measurements gives strong support to the assertion that, for the mass spectrometers of this laboratory, the observed bias is independent of isotopic composition and is primarily a function of evaporation and ionization in the source; a single correction factor is valid within the linear response region of the measuring circuit.

For ^{233}U isotope dilution no significant systematic differences were observed for extra SRM samples spiked at each change in dilution of the stock "U233" solution. A comparison of minor isotopic composition by ion multiplier detection and by conventional detection with a "Z" source for the SRMs U-200, U-150 and U-100, indicated no systematic differences, and thus, an accurate correction for the additional bias effects of ion multiplier measurements was made. Multiplier measurements were also more imprecise than conventional detection with the "Z" lens source. The "Z" lens source made it possible to use the conventional NBS collector in determining the minor isotopic composition of all SRMs except U-020 through U-005 and the ^{234}U composition of SRM U-0002.

Analysis of unspiked SRMs, as control samples, along with the spiked SRMs revealed that minor isotopic composition for the unspiked samples was systematically greater (∿0.2%) than the isotope dilution values. This apparent enrichment was attributed to a non-linear effect of the measuring circuit when comparing such large ion current ratios. When the minor isotope composition of SRMs U-500 through U-030 were redetermined using the "Z" lens source, unspiked solutions were again analyzed as control samples but with special precautions to minimize the effects of non-linear response. The values of the VRE decade resistors were carefully checked, the ^{235}U signal intensity was maintained below non-ohmic response levels and the magnet scan rate was reset to give approximately one minute between peak tops. The isotopic composition of the unspiked samples was again greater than the isotope dilution values but the difference was less than 0.1 percent. On the basis of these and a limited number of subsequent measurements it is believed that nearly all of the original difference between the spiked and unspiked data is caused by a R-C response contribution for an ion current ratio of 100.

SRM U-970 was the only sample for which an attempt was made to determine ^{238}U composition by isotope dilution, and was also the only effort to measure ^{234}U with a spike that was not approximately the same magnitude. This limited test gave no indication of dependence of ^{234}U composition on the magnitude of the spike. The ^{233}U isotope dilution of the SRMs was inferior to the point calibration technique of determining ^{238}U composition because of the detrimental effect of propagating small systematic errors (∿0.02% per mass unit) over a 5 mass unit range. For highly enriched ^{235}U samples in which the ^{238}U composition is at the parts per million level, isotope dilution may offer some advantages in spite of the error propagation.

The certified composition (atom percent) of the uranium SRMs is given in Tables 40 and 41. All of the ^{234}U and ^{236}U values are the results of NBS determinations by ^{233}U isotope dilution. The ^{235}U and ^{238}U values were calculated, where applicable, from point calibration measurements of the ^{235}U/^{238}U ratio at NBS. For SRMs with ^{235}U/^{238}U ratio determinations at NBS using the systems calibration technique, the values of NBS, GAT and UCNC were given equal weight and averaged to yield a certified value. Some small and statistically insignificant differences between minor isotope values in the certified data tables and the NBS data of Table 38 exist, because once a certificate is issued, it is not reissued to reflect shifts of a few parts in ten thousand as additional data is accumulated. The uncertainty statement for the isotopic SRMs is the 95% confidence limits for a single determintion because this is the limiting error statement that can be made for an isotopic measurement and is always approximately equal to the overall limit of error. The overall limit of error is the sum of the 95% confidence limits for the ratio determination and other

Table 40. Certified atom percent composition of SRMs U-0002 through U-150.

SRM	^{234}U	^{235}U	^{236}U	^{238}U
U-0002	0.00016 ±.00001	0.01755 ±.00005	<0.00001	99.9823 ±.0001
U-005	0.00218 ±.00004	0.4985 ±.0005	0.00466 ±.00005	99.504 ±.001
U-010	0.00541 ±.00005	1.0037 ±.0010	0.00681 ±.00007	98.984 ±.001
U-015	0.00850 ±.00009	1.5323 ±.0015	0.0164 ±.0001	98.443 ±.002
U-020	0.0125 ±.0001	2.038 ±.002	0.0165 ±.0001	97.933 ±.002
U-030	0.0190 ±.0001	3.046 ±.003	0.0204 ±.0001	96.915 ±.003
U-050	0.0279 ±.0001	5.010 ±.005	0.0480 ±.0002	94.915 ±.005
U-100	0.0676 ±.0002	10.190 ±.010	0.0379 ±.0001	89.704 ±.010
U-150	0.0993 ±.0002	15.307 ±.015	0.0660 ±.0002	84.528 ±.015

Table 41. Certified atom percent composition of SRMs U-200 through U-970.

SRM	^{234}U	^{235}U	^{236}U	^{238}U
U-200	0.1246	20.013	0.2116	79.651
	±.0003	±.020	±.0006	±.021
U-350	0.2498	35.190	0.1673	64.393
	±.0006	±.035	±.0005	±.036
U-500	0.5181	49.696	0.0755	49.711
	±.0008	±.050	±.0003	±.050
U-750	0.5923	75.357	0.2499	23.801
	±.0009	±.025	±.0008	±.024
U-800	0.6563	80.279	0.2445	18.820
	±.0013	±.021	±.0007	±.019
U-850	0.6437	85.137	0.3704	13.848
	±.0014	±.017	±.0011	±.014
U-900	0.7777	90.196	0.3327	8.693
	±.0015	±.011	±.0010	±.008
U-930	1.0812	93.336	0.2027	5.380
	±.0020	±.010	±.0006	±.005
U-970	1.6653	97.663	0.1491	0.5229
	±.0017	±.003	±.0005	±.0006

known sources of possible systematic error and is determined by performing the necessary experimentation to evaluate each bias component. The overall limit of error has also been determined for boron [5], rubidium [6], copper [13], magnesium [14], chromium [15], silver [16], chlorine [17], bromine [18] and lead [19] as part of the NBS absolute isotopic abundance and atomic weight program. For each of these elements the magnitude of the overall limit of error is approximately the same as the 95% confidence limits for a single ratio determination. Thus, usage of the confidence limits for a single determination to establish a minimum error statement which approximates the summation of all uncertainty components commonly associated with NBS isotopic abundance measurements is based on an extensive volume of experimental data.

ACKNOWLEDGMENTS

We are indebted to the following: John L. Hague, Inorganic Standards Coordinator, for his role in establishing the uranium chemistry laboratory and for his counsel in developing the uranium chemical procedures; Mrs. Martha S. Richmond for assistance with the preparation of most of the ^{233}U isotope dilution samples; Mrs. Joy Shoemaker for skill, dedication and infinite patience in typing and assembling the manuscript.

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APPENDIX I

The "NBS type" 12-inch radius of curvature 68° analyzer tube mass spectrometer with the combinations of components that were standard instrumentation from 1960 through 1970 is shown in Figures 9, 10 and 11. Initially, the 12-inch instrument (Figure 9) had differential pumping of the source housing and analyzer tube by mercury diffusion pumps. Gate valves isolated the pumping system so that venting of the source and analyzer tube to atmospheric pressure was accomplished without loss of vacuum in the diffusion pumps. Both the source and collector [9] had slit assemblies that were externally adjustable by means of a micrometer screw.

A major modification in the instrumentation of the 12-inch mass spectrometer during the 1963-1966 period was replacement of the analyzer tube diffusion pump with an electronic pump (Figure 10). Other significant changes adopted as standard instrumentation were a cryogenic pump (coldfinger) in the source housing and a small diameter window in the source housing flange.

Figure 11 shows the standard instrument during the 1966-1970 period. The major modifications include the following: replacement of the gate valves by air-operated valves [11]; installation of a high vacuum beam valve [10,11]; the use of a slot type mount for both the source and collector [10]; elimination of the externally adjustable slit assembly of the collector and source; and the use of a "Z" lens source [10].

The "NBS type" 90°, 12-inch radius extended flight path mass spectrometer is shown in Figure 12. The magnet and analyzer tube are identical to the first stage of the multi-stage mass spectrometer [10] developed several years ago. The analyzer tube is mounted in a horizontal plane and is pumped by a double-ended electronic pump. An air-operated beam valve is located immediately behind the source housing and is closed except when an analysis is made. The source housing is pumped by a mercury diffusion pump and is isolated from the pump by another air operated valve. The source [10], collector [10], expanded scale measuring circuit [9] and the other electronic components are interchangeable with the corresponding components of the 68° instrument.

The analytical performance of the 90° mass spectrometer matches or exceeds that of the "work horse" 68° instrument in all practical aspects. The 90° instrument has greater transmission efficiency and nearly the same dispersion as the 68° spectrometer. In addition, all components of the 90° instrument are serviceable with the operator standing on the floor. The most recent innovation, locating the filament control panel in the console so that the operator can simultaneously view the ionizing filament with the pyrometer and adjust the filament current to obtain a given temperature, is shown in Figure 12. The 1971 version of the 12-inch 68° analyzer tube mass spectrometer has been modified to include this feature but will not be completed in time for a photograph to be prepared for this publication. This modification is a direct result of the increased use of the optical pyrometer in measuring the temperature of the ionizing filament. Pyrometer measurement is the exclusive method of reproducing an optimum temperature for the ionizing filament for all triple filament analyses. All of the current single filament procedures - boron, chromium, lead and nickel - are based exclusively on adjusting to temperatures measured with the optical pyrometer rather than ion current intensity or current through the filament. Since the introduction of the window in the source housing flange, the use of the pyrometer has increased until it is now an integral part of all mass spectrometric analytical procedures.

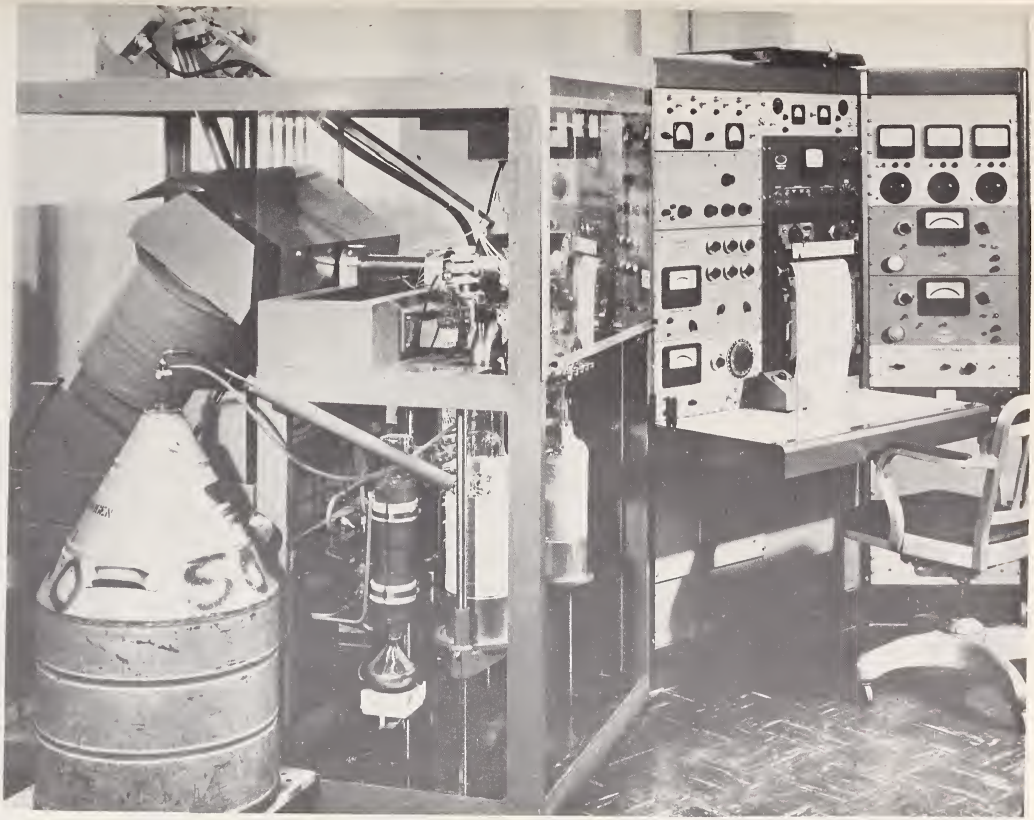

Figure 9. 12-inch radius of curvature 68° analyzer tube mass spectrometer from 1960 to 1963.

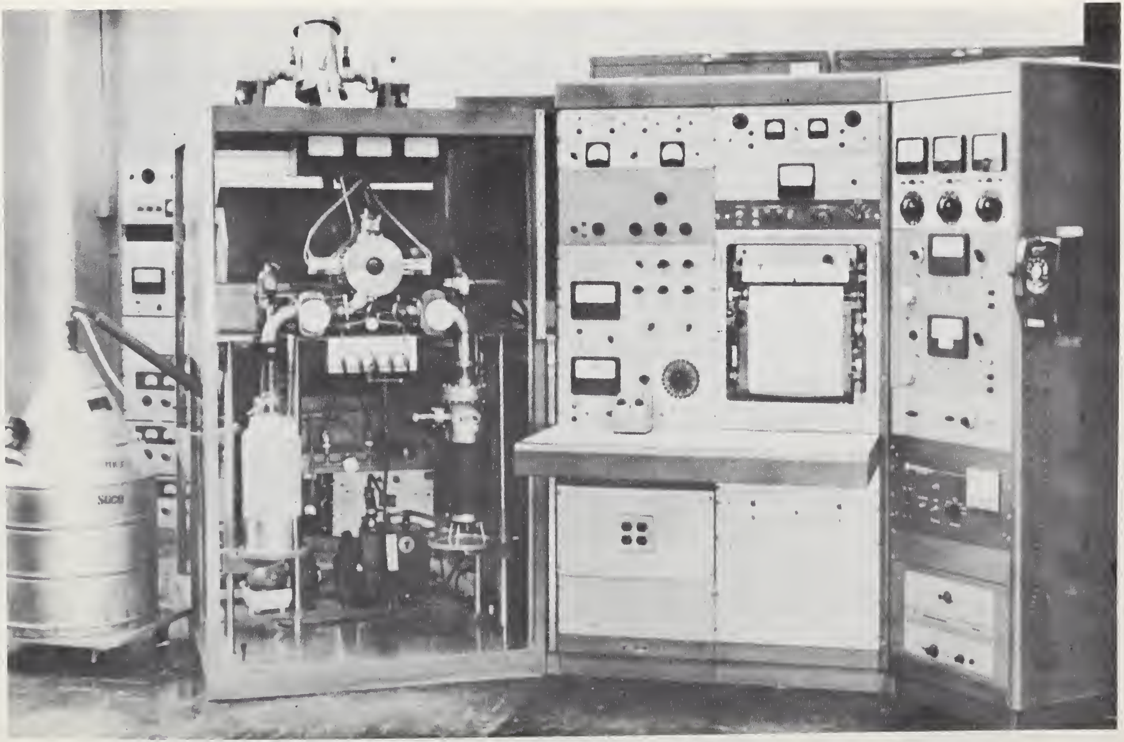

Figure 10. 12--inch radius of curvature 68° analyzer tube mass spectrometer from 1963 to 1966.

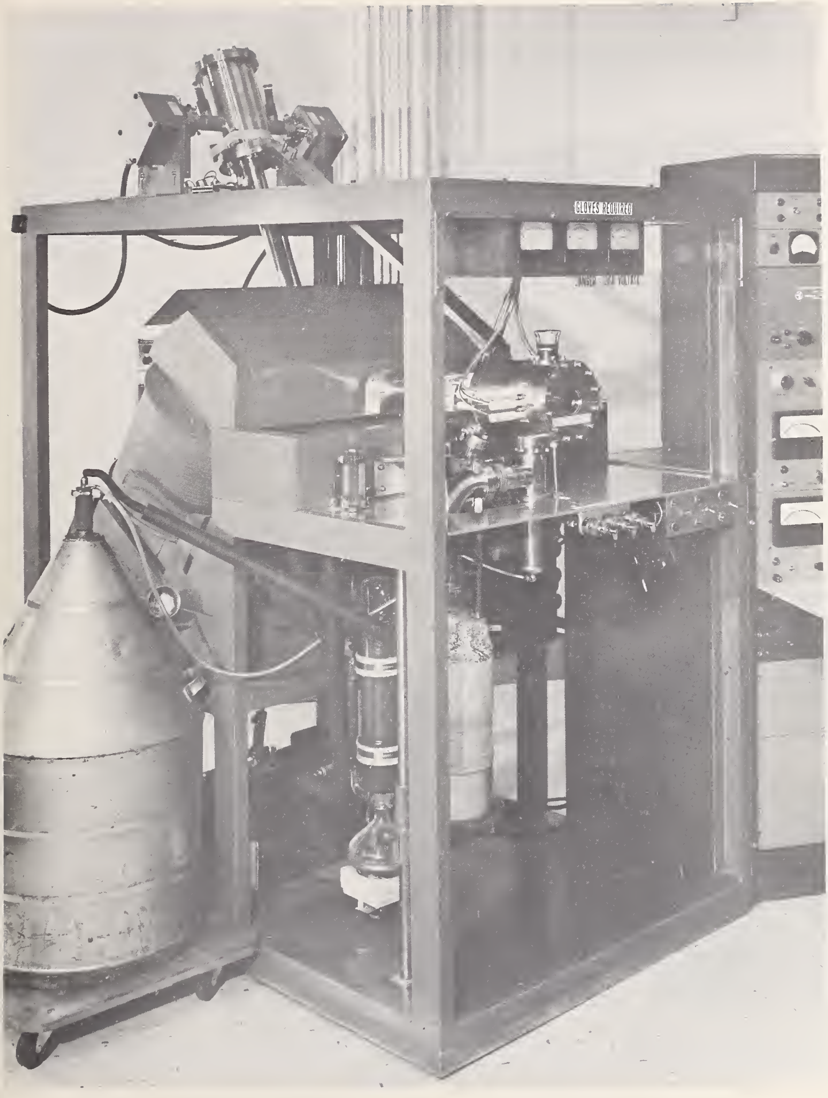

Figure 11. 12-inch radius of curvature 68° analyzer tube mass spectrometer from 1966 to 1970.

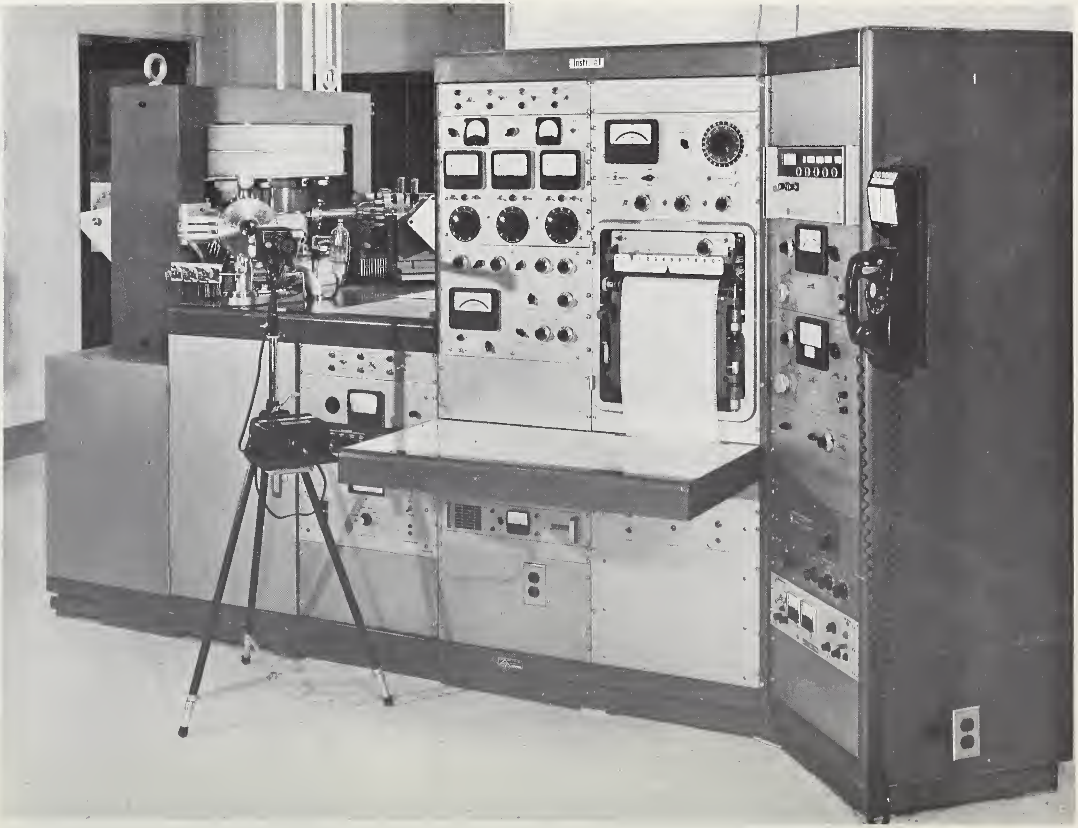

Figure 12. 12-inch radius of curvature 90° analyzer tube mass spectrometer.

APPENDIX II

CERTIFICATES OF ANALYSIS

Uranium Isotopic Standard:

J. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL U-0002

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom Percent	0.00016	0.01755	<0.00001	99.9823
	± .00001	± .00005	- - - - - - -	± .0001
Weight Percent	.00016	.01733	< .00001	99.9825

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 238.0503 using the nuclidic masses 234.0409; 235.0439; and 238.0508.

The value for ^{235}U is calculated from measurements made on samples spiked with high purity ^{233}U to approximate the ^{235}U concentration, the ratio ^{233}U to ^{235}U was measured on a triple-filament equipped thermal ionization mass spectrometer with d-c amplifier circuits. Ratio determinations were corrected for mass discrimination by measurements made under similar conditions on SRM U-500.

The value for ^{234}U is calculated from measurements made on samples spiked with high purity ^{233}U, the ratio ^{233}U to ^{234}U was measured on a two stage mass spectrometer using a pulse counting technique.

The limits indicated for the isotopic compositions are at least as large as the 95 percent confidence level for a single determination, and include terms for the inhomogeneities of the material as well as analytical error.

Mass spectrometry measurements at NBS were made by E. L. Garner and L. J. Moore using solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
July 30, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material U-005
Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.00218	0.4895	0.00466	99.504
	±.00004	±.0005	±.00005	±.001
Weight percent	0.00214	0.4833	0.00462	99.510

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 238.036 using the nuclidic masses 234.0409; 235.0439; 236.0457 and 238.0508.

The values for ^{234}U and ^{236}U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements of the ^{235}U to ^{238}U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with dc amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 0.5 percent ^{235}U level from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 0.004919, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner on solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of March 2, 1959)

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material U-010

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.00541	1.0037	0.00681	98.984
	±.00005	±.0010	±.00007	±.001
Weight percent	0.00532	0.9911	0.00675	98.997

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 238.020 using the nuclidic masses 234.0409; 235.0439; 236.0457 and 238.0508.

The values for ^{234}U and ^{236}U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements of the ^{235}U to ^{238}U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with dc amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 1 percent ^{235}U level from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 0.010140, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner on solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of March 2, 1959)

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material U-015

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.00850	1.5323	0.0164	98.443
	±.00009	±.0015	±.0001	±.002
Weight percent	0.00836	1.5132	0.0163	98.462

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 238.004 using the nuclidic masses 234.0409; 235.0439; 236.0457 and 238.0508.

The values for ^{234}U and ^{236}U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements of the ^{235}U to ^{238}U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with dc amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 1.5 percent ^{235}U level from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 0.015565, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner on solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of October 1, 1958)

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material U-020
Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.0125	2.038	0.0165	97.933
	±.0001	±.002	±.0001	±.002
Weight percent	0.0123	2.013	0.0164	97.959

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 237.989 using the nuclidic masses 234.0409; 235.0439; 236.0457 and 238.0508.

The values for ^{234}U and ^{236}U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements of the ^{235}U to ^{238}U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with dc amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 2 percent ^{235}U level from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 0.02081, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner on solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of October 1, 1958)

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material U-030

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.0190	3.046	0.0204	96.915
	±.0001	±.003	±.0001	±.003
Weight percent	0.0187	3.009	0.0202	96.953

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 237.958 using the nuclidic masses 234.0409; 235.0439; 236.0457 and 238.0508.

The values for ^{234}U and ^{236}U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements of the ^{235}U to ^{238}U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with dc amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 3 percent ^{235}U level from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 0.03143, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner on solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of October 1, 1958)

S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate

Standard Reference Material U-050
Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.0279	5.010	0.0480	94.915
	±.0001	±.005	±.0002	±.005
Weight percent	0.0275	4.949	0.0476	94.975

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 237.898 using the nuclidic masses 234.0409; 235.0439; 236.0457 and 238.0508.

The values for ^{234}U and ^{236}U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements of the ^{235}U to ^{238}U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with dc amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 5 percent ^{235}U level from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence limits for a single determination, and include terms for inhomogeneities in the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 0.05278, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner on solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
April 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of October 1, 1958)

U. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-100

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.0676	10.190	0.0379	89.704
	±.0002	±0.010	±.0001	±0.010
Weight percent	.0666	10.075	.0376	89.821

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 237.741 using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements made at the National Bureau of Standards of the ^{235}U to ^{238}U ratio. The observed ratios were corrected for mass discrimination effects by intercomparison with five synthetic mixtures at the 10-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 0.11360, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
June 23, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supercedes certificate of 7-1-59)

. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-150

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.0993	15.307	0.0660	84.528
	±.0002	±0.015	±.0002	±0.015
Weight percent	.0978	15.143	.0656	84.693

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 237.585 using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-100. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{235}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{238}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 0.18109, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

Washington, D.C. 20234
August 5, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 7-1-59)

U. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-200

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.1246	20.013	0.2116	79.651
	±.0003	±0.020	±.0006	±0.021
Weight percent	.1229	19.811	.2103	79.856

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 237.440 using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-100. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{235}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{238}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 0.25126, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
June 1, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 10-1-58)

S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-350

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.2498	35.190	0.1673	64.393
	±.0006	±0.035	±.0005	±0.036
Weight percent	.2467	34.903	.1667	64.684

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 236.979, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-100. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{235}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{238}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 0.5465 is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
May 23, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 3–2–59)

U. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-500

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.5181 ±.0008	49.696 ±0.050	0.0755 ±.0003	49.711 ±0.050
Weight percent	.5126	49.383	.0754	50.029

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 236.534, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements made at the National Bureau of Standards of the ^{235}U to ^{238}U ratio. The observed ratios were corrected for mass discrimination effects by intercomparison with five synthetic mixtures at the 50-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 0.9997, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
May 24, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 12–16–63)

S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-750

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.5923	75.357	0.2499	23.801
	±.0009	±0.025	±.0008	±0.024
Weight percent	.5880	75.129	.2502	24.033

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 235.756, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-900. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{238}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{235}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 3.166, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
February 11, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 3-2-59)

U. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-800

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.6563 ±.0013	80.279 ±0.021	0.2445 ±.0007	18.820 ±0.019
Weight percent	.6519	80.088	.2450	19.015

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 235.606, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-900. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{238}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{235}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 4.266, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
February 11, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 3-6-59)

. Department of Commerce
hn T. Connor, Secretary
tional Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-850

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.6437	85.137	0.3704	13.848
	±.0014	±0.017	±.0011	±0.014
Weight percent	.6399	84.988	.3713	14.001

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 235.458, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-900. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{238}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{235}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 6.148, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
February 11, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 10-1-58)

U. S. Department of Commerce
John T. Connor, Secretary
National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-900

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	0.7777	90.196	0.3327	8.693
	±.0015	±0.011	±.0010	±0.008
Weight percent	.7735	90.098	.3337	8.795

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 235.301, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U were calculated from measurements made at the National Bureau of Standards of the ^{235}U to ^{238}U ratio. The observed ratios were corrected for mass discrimination effects by intercomparison with five synthetic mixtures at the 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 10.375, is known to at least 0.1 percent.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
February 11, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 10-1-58)

Department of Commerce
n T. Connor, Secretary
ional Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material U-930

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom percent	1.0812	93.336	0.2027	5.380
	±0.0020	±0.010	±.0006	±0.005
Weight percent	1.0759	93.276	.2034	5.445

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 235.197, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity ^{233}U to approximate the ^{234}U concentration, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for ^{235}U and ^{238}U are derived from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the ^{235}U to ^{238}U ratio using triple filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-900. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent ^{235}U level prepared from high-purity ^{235}U and ^{238}U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent ^{235}U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the ^{238}U concentration by oxide dilution and UF_6 analysis, and then the ratio calculated using the NBS values for ^{234}U and ^{236}U, and the ^{235}U value obtained by difference.

The limits indicated for the isotopic concentrations are at least as large as the 95-percent confidence level for a single determination. The ^{235}U to ^{238}U ratio for this standard, 17.349, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Mass spectrometry measurements at NBS were made by Ernest L. Garner and William R. Shields on solutions prepared by Lawrence A. Machlan and Martha S. Richmond.

WASHINGTON, D.C. 20234
February 11, 1966

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(This certificate supersedes certificate of 12-1-58)

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL U-970

Uranium Isotopic Standard

	^{234}U	^{235}U	^{236}U	^{238}U
Atom Percent	1.6653	97.663	0.1491	0.5229
	±0.0017	±0.003	±0.0005	±0.0006
Weight Percent	1.6582	97.663	0.1497	0.5296

The material consists of highly purified oxide, U_3O_8. The atomic weight of the material is calculated to be 235.045, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for ^{234}U and ^{236}U are calculated from measurements made on samples spiked with high purity ^{233}U to approximate the ^{234}U and ^{236}U concentrations, the ratios ^{233}U to ^{234}U and ^{233}U to ^{236}U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits. Ratio determinations were corrected for mass discrimination by measurements made under similar conditions on SRM U-500.

The value for ^{238}U is calculated from measurements of the ratio ^{235}U to ^{238}U, and calibrated by measurements of the same ratio on synthetic mixtures prepared from high-purity separated isotopes of ^{235}U and ^{238}U to approximate the composition of the sample. Because of the response time of the measuring circuit when switching from the ^{235}U peak to the ^{238}U peak, the ^{238}U peak was monitored for 1 minute and only data from the last 30 seconds, after the signal had stabilized, was used in the calculations. The value for ^{235}U is calculated by difference.

The limits indicated for the isotopic compositions are at least as large as the 95 percent confidence level for a single determination, and include terms for the inhomogeneities of the material as well as analytical error. The ^{235}U to ^{238}U ratio for this standard, 186.78, is known to at least 0.15 percent.

Mass spectrometry measurements at NBS were made by E. L. Garner using solutions prepared by L. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
July 9, 1970

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

Latest developments in the subject area of this publication, as well as in other areas where the National Bureau of Standards is active, are reported in the NBS Technical News Bulletin. See following page.

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