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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

Uranium-235 Isotope Abundance Standard Reference Materials for Gamma Spectrometry Measurements

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PREFACE

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are "well-characterized materials, produced in quantity, that calibrate a measurement system to assure compatibility of measurement in the Nation." SRM's 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 SRM's. 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 in arriving at the certified values and of procedures used in producing SRM's. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series is reserved for the purpose.

This 260 Series is dedicated to the dissemination of information on all phases of the preparation of the NBS uranium isotopic SRM for nondestructive assay. In general, much more detail will be found in this 260 than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity of processes employed, and to learn details of methods utilized for work entailing the greatest care. It is hoped that this 260 will provide sufficient additional information not found on the certificate so that new applications of these SRM's may be found.

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

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ABSTRACTS

The accurate determination of isotope abundances by any method requires that the measuring systems be calibrated using well characterized isotope reference materials. The National Bureau of Standards (NBS) and the Central Bureau for Nuclear Measurements (CBNM) have jointly produced and certified U_3O_8 nondestructive assay (NDA) reference samples to be used for calibrating gamma measurements. Five different uranium abundances have been certified (0.31, 0.71, 1.95, 2.95, and 4.46 nominal mass percent, $^{235}U/U$). In this 260 series publication, the material fabrication and certification are described and a discussion of the measurement results affecting the accuracy of gamma spectrometry is given. These certified standards represent the first example of an international effort that establishes traceability to NBS, CBNM, and the basic SI units.

Key words: gamma energy; gamma spectrometry; homogeneity; mass spectrometry; nondestructive assay; reference material; specifications aluminum; uncertainty; $^{235}U/U$ isotope abundances.

DISCLAIMER

Certain chemicals, commercial equipment, or instruments are identified in this document in order to adequately specify the experimental procedure. In no cases does such materials identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment is necessarily the best available for the purpose.

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1. Introduction

The traditional technique for uranium isotope abundance measurements is a destructive assay using mass spectrometry. In recent years, a number of studies have explored use of gamma spectrometry, a nondestructive method of assay. This method offers a number of advantanges. The cost for the equipment and the analysis are substantially less than the mass spectrometry cost. The equipment can be made portable for in-field measurements, and analysis time is short thereby allowing quick turn-around of results for possible safeguard applications. In addition, substantial improvements in the accuracy of this method have been made with the use of Certified Reference Materials (CRM), referred to by the National Bureau of Standards as Standard Reference Materials (SRMs). This report describes the development of these (CRMs) and the improved accuracy observed with the use of the CRMs in a measurement system.

To assure high quality measurements by any methods, it is necessary to have available accurately certified reference materials similar in composition to the materials that are commonly measured. This is particularly true of gamma spectrometry SRMs. In this case, the material must be in the form of a chemically and isotopically homogeneous uranium layer that is carefully adjusted for density and thickness as required when using the 185.7 keV gamma-line of ^{235}U for measurements (1-3). When measured under well defined conditions as described in this report, the counting rate of this gamma line is proportional to the ^{235}U isotopic abundance.

In a joint research inititative between the National Bureau of Standards (NBS) and the Central Bureau for Nuclear Measurements (CBNM) Geel Belgium, an SRM for nondestructive assay of uranium materials using gamma spectrometry has been developed. This SRM consists of a set of five U_3O_8 powders separately encased in special designed aluminum cans. The nominal $^{235}U/U$ mass abundances are 0.0031, 0.0071, 0.0194, 0.0295, and 0.0446, respectively. These materials were characterized and certified by CBNM and NBS, with supporting measurements from the Department of Energy New Brunswick Laboratory. NBS will issue these materials as SRM 969 and CBNM will issue them as EC NRM 171, with a certification report (COM 4153) which is the equivalent to this NBS 260 publication.

This publication describes the material fabrication, a discussion of parameters that affect the measurement accuracy by gamma spectrometry, and the procedures for proper use of the SRM (4,5).

2. Description and Intended Use

Standard Reference Material (SRM) 969 consists of a set of five uranium oxide (U_3O_8) samples in aluminum cans, with isotope mass ratios of uranium-235 to total uranium ($^{235}U/U$) equal to 0.0031, 0.0071, 0.0194, 0.0295, and 0.0446 (referred to as samples or materials 031, 071, 194, 295, and 446 respectively). Each can (see Figure 1) contains 200.1 g of U_3O_8 as a pressed powder layer with a diameter of 70 mm. A mean U_3O_8 specific mass over the sample surface of 5.2 g/cm^2 was achieved with sample heights of approximately 2.0 cm for all samples with the exception of 446 which has a height of 1.5 cm.

A surface density of 5.2 g/cm^2 ensures that the characteristic 185.7 keV gamma-radiation of ^{235}U, which is emitted through the can "window", is at least 99.9% of the emission rate that can be obtained from an infinitely thick source. The radiation is normally detected using a high-resolution gamma detector for which a defined viewing angle is chosen with the use of a suitable lead (Pb) collimator (see Figure 2).

The intended use of this SRM is to provide scientists using gamma spectrometry a basis for accurate and worldwide accepted calibrations of isotope abundance measurements on uranium materials. These samples can be used to calibrate working standards or plant-specific reference materials. Care must be taken to ensure that the measurement of a material with an unknown abundance, be performed with the same detector-collimator configuration as the reference material. In addition, the use of sufficiently thick as well as chemically pure uranium layers, homogeneous with respect to their ^{235}U abundance and chemical composition, are required (see details in the User's Manual) (5).

The unknown abundance (A_u) of a uranium material is obtained from gamma counting and from the abundance (A_r) of a reference material by using the following equation:

$$A_u = A_r[(K_gC)_u/(K_gC)_r]\ K_m\ K_s\ K_c \qquad (1)$$

C_u, C_r are the photo-peak counting rates for the 185.7 keV line determined from the gamma spectra of both the unknown and the reference samples (see typical spectra in Figure 3).

K_{gu}, K_{gr} are small corrections of photo-peak counting rates for most of the unresolvable gamma lines near 185.7 keV, such as the protactinium daughter products of ^{238}U (6,7).

$$(K_g)_u = 1-\emptyset/A_u,\quad (K_g)_r = 1-\emptyset/A_r \qquad (2)$$

where $\emptyset$, which is $<1.15 \times 10^{-5}$, is the bias associated with the age of the uranium sample from last chemical separation; for older samples, $\emptyset$ approaches zero. The K values allow correction for differences between the unknown and the reference materials with respect to the chemical composition of the uranium materials (K_m), is related to the surface density of the uranium samples compared to "infinite thickness" (K_s), and is related to the material type and the thickness of the can "window" (K_c).

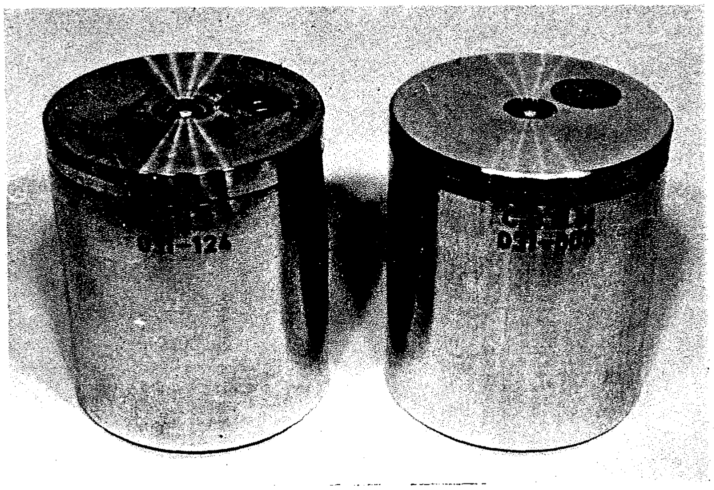


Figure 1. ^{235}U Isotope Abundance Certified Reference Material Samples for Non-destructive Gamma Spectrometry

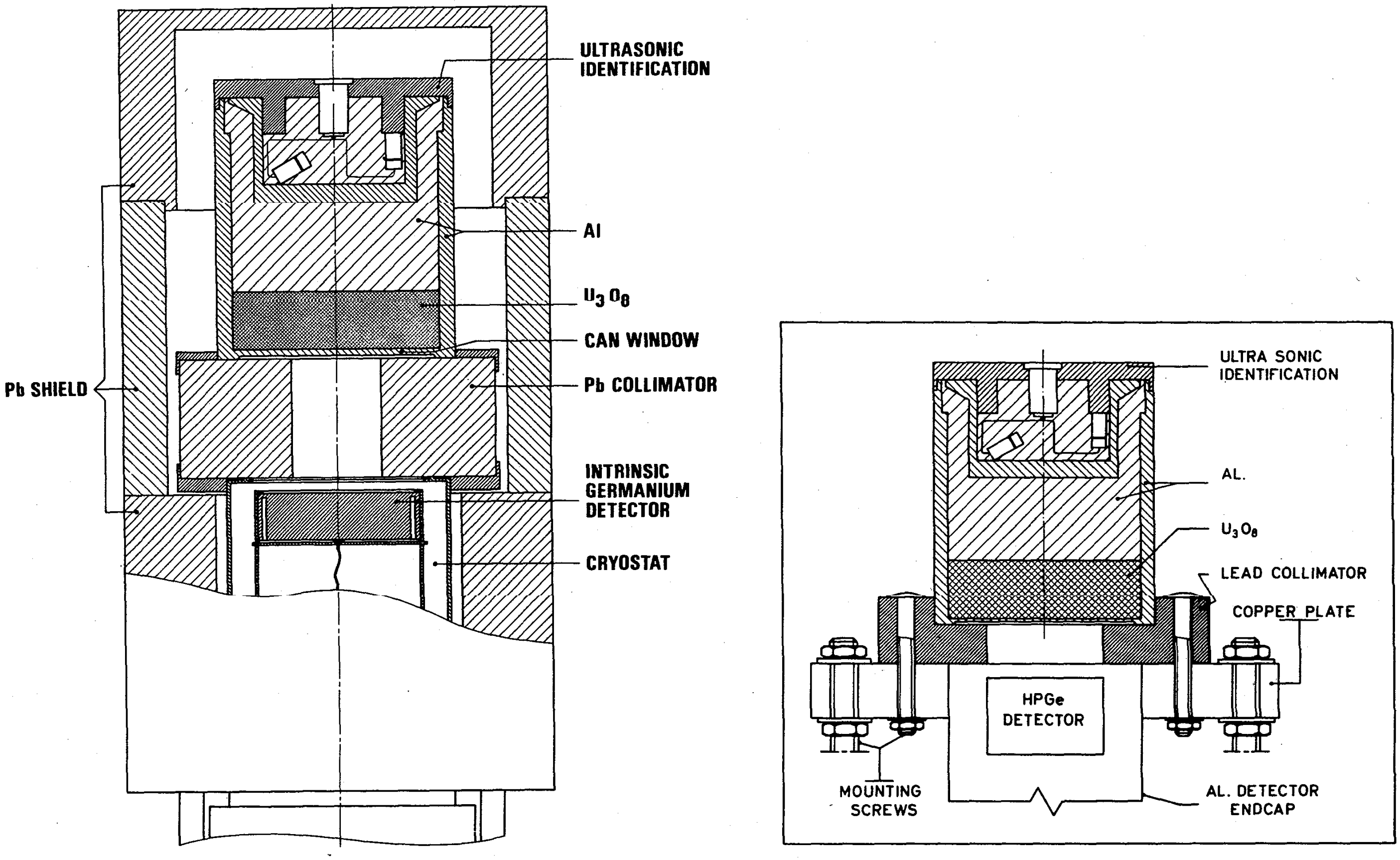


Figure 2. Set-up for Gamma Spectrometry for Counting U_3O_8 Reference Samples a) used by CBNM b) used by NBS

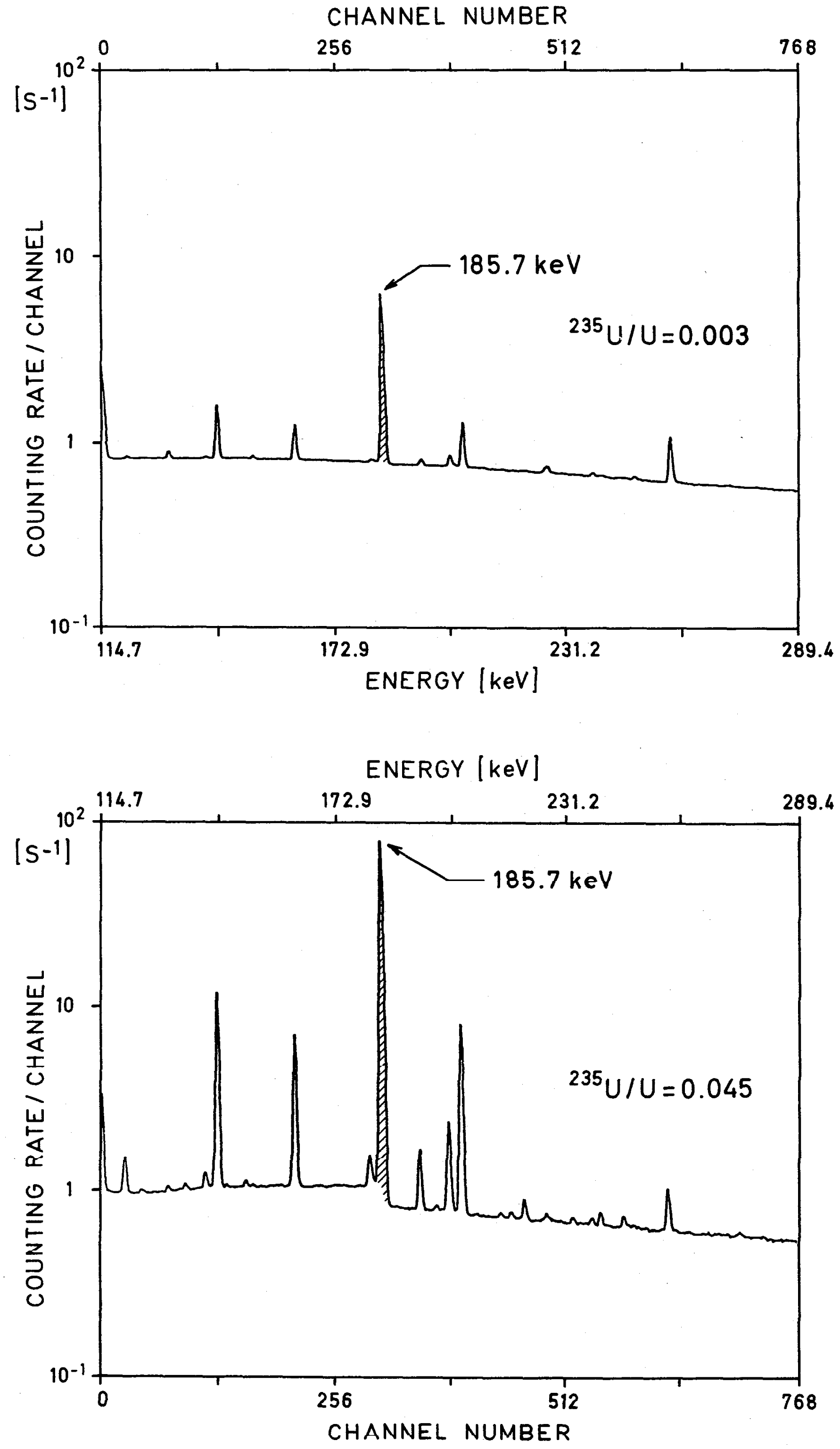


Figure 3. Gamma Spectra of U_3O_8 Reference Samples Measured with a High Resolution Germanium Detector

An empty aluminum can, identical to the ones used for the reference samples, is supplied with each set of reference materials to facilitate the measurement of unknown materials. When this can is used $K_c = 1$.

The reference materials are identified by numbers engraved in the wall of the cans as shown in Figure 1. The numbers indicate the issuing organization, a three digit number for the ^{235}U abundances (in weight percent X 100), and a three digit sequential number common to each set.

In addition, all individual sample cans are equipped with a unique and tamper-proof seal inserted into the top part of the can. For identification, a special ultrasonic transceiver is used which can read the ultrasonic fingerprint in the seal via the connector on the cover of the cans (see Reference 5 and 8). Using this fingerprint, a verification of the signature of each sample can is possible for safeguards purposes.

3. Preparation of the Reference Samples

The main steps in the fabrication procedure were:

- Fabrication of cans and plugs to the required dimensional tolerances
- Acceptance control of cans and plugs
- Filling of cans with U_3O_8 powder and accurate mass definition
- Sampling for production control
- Pressing of the U_3O_8 powder
- Automatic Tungsten Inert Gas (TIG) welding of the plug onto the can
- Final dimensional check and adjustment of the window flatness of the can.

Emphasis was placed on extensive control and inspection throughout the fabrication process to guarantee the required specifications.

3.1 Fabrication of Cans and Plugs

The cans and plugs were machined from solid rod base materials at NBS using an automatic lathe. Since the windows could not be made to conform to required tolerances on the automatic lathe, they were machined with an overthickness of 0.07 mm, then adjusted to the required tolerance at CBNM by further machining.

Dimensions and tolerances of the can and plug are given in Figure 4.

The material used for the preparation of cans and plugs is ASTM 6061-T6 aluminum alloy with the following impurity specifications (values in units of mass %):

Si : 0.4 - 0.8	Mg : 0.8 - 1.2	Mn : $\leq$ 0.15
Cu : 0.15 - 0.4	Fe : $\leq$ 0.7	Ti : $\leq$ 0.15
Cr : 0.04 - 0.35	Zn : $\leq$ 0.25	U : < 0.00025

Other elements : each $\leq$ 0.05
: total $\leq$ 0.15

It should be noted that the 2.5 $\mu g/g$ of uranium in the aluminum can material will affect gamma measurements by less than 3 parts in 10^6 for depleted uranium with $^{235}U/U = 0.0031$.

The control measurements as well as the selection of the cans and plugs are described in this text.

All metrological data pertinent to a particular can is provided with each reference material container. For an example see Figure 5.

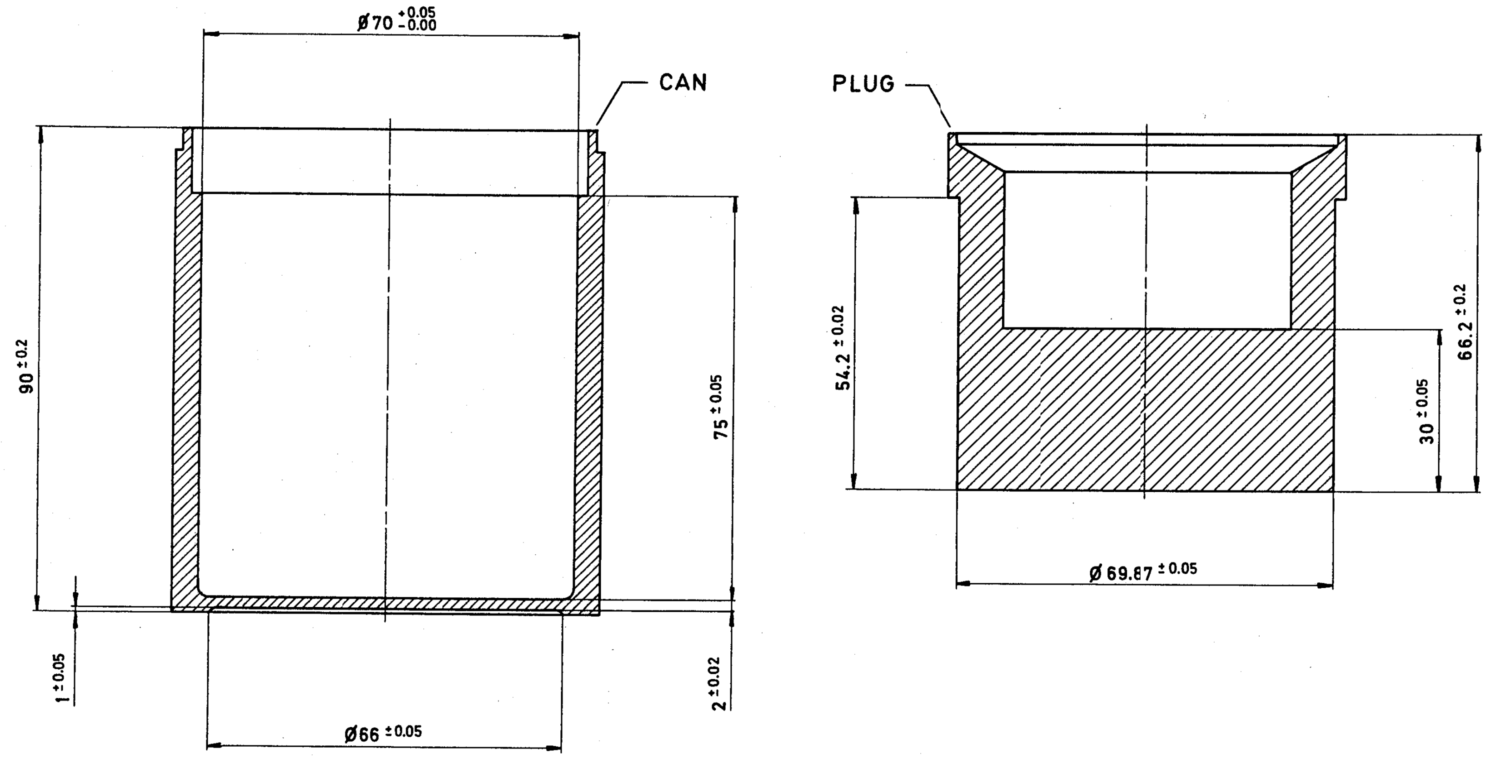


Figure 4. Dimensions and Tolerances of the U_3O_8 NDA Reference Material Cans.
Material: Al-alloy ASTM 6061-T6

Container N°: CBNM 194-024
Tot. Mass U_3O_8: (200.1 ±0.2)g
A: 54.20 mm
B: 11.98
C: 30.00
ϕ_w: 69.88

d: 1.989
H: 88.98
j: 1.01
ϕ_x: 70.03
ϕ_y: 66.0
ϕ_z: 79.95

D: 52.77
E: 20.78

f: < 0.1 (Bottom Flatness)

Bottom thickness:	1	2.002 mm
	2	2.005
	3	2.000
	4	2.003
	5	2.000
	6	1.996
	7	2.001
	8	2.000
	9	1.985
	10	1.987
	11	1.986
	12	1.979
	13	2.006
	$\bar{x}_{13}$	1.996
	s_{13}	0.009 (All *areas*)
	$\bar{x}_5$	1.989
	x_5	0.010
	(Five inner areas)	

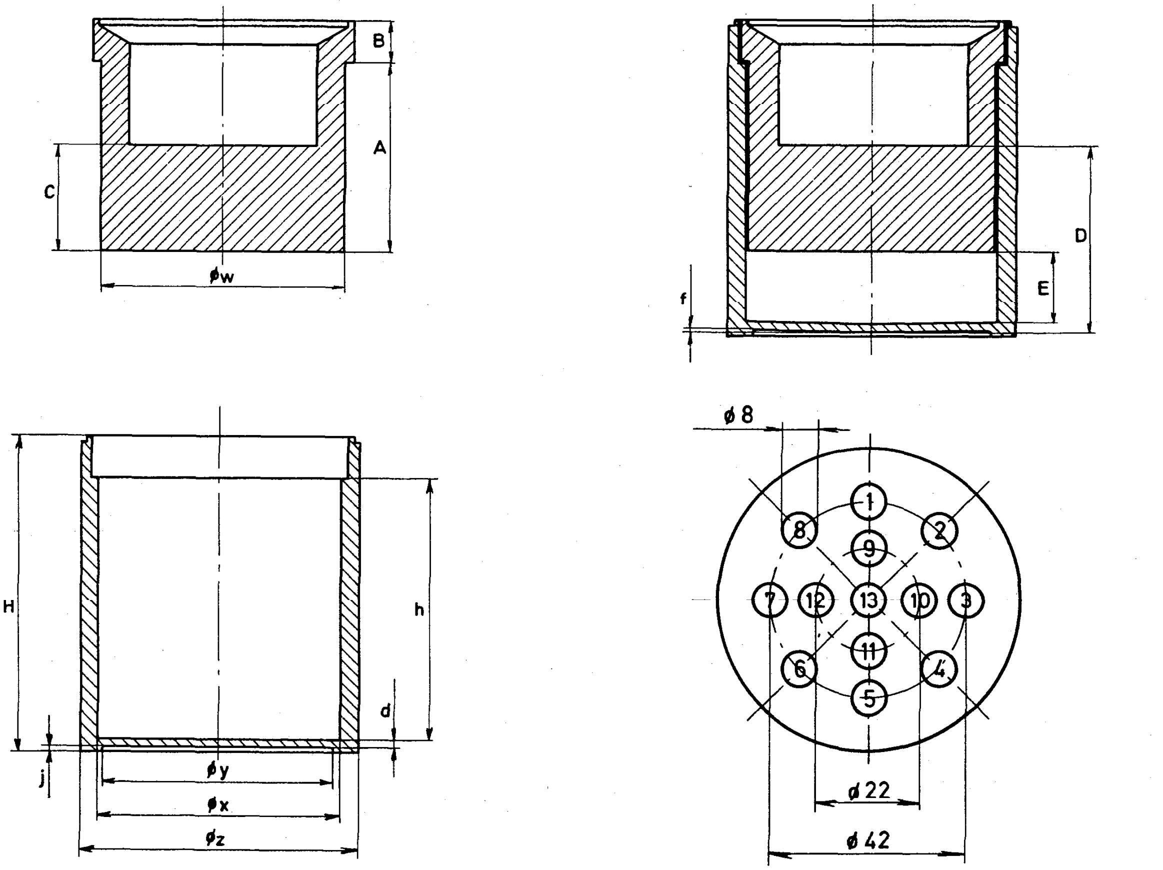


Figure 5. Example of Dimensional Control of Can and Window with All Dimensions Given in mm

3.2 Filling the Cans with U_3O_8 Powder

The required amount of U_3O_8 (200.1 ± 0.2g) was weighed into the can and pressed to 3 mm above the required final thickness by means of a steel plug using a hydraulic press (diameter of steel plug = 69 mm, inner diameter of can = 70 mm so that air could escape during pressing). A surface density of 5.2 g/cm^2 was achieved.

The U_3O_8 in the gap between the plug and the wall of the can was carefully brushed back into the can and the U_3O_8 mass adjusted. This pressing was performed twice. The permanent Al plug was then placed into its final position such that the lips of the plug and the can were pressed together. To avoid deformation, the can was tightly fitted into a recess in a heavy steel block during the entire hydraulic pressing procedure.

The U_3O_8 masses were determined using a Mettler balance type PC 2000 with a capacity of 2100 g, a reproducibility of ±0.01 g and a linearity of ±0.015 g. The balance was calibrated daily with a test weight calibrated against the CBNM standard kilogram. The indicated uncertainty of ±0.2 g on the U_3O_8 mass includes all sources of error.

The four U_3O_8 materials (031; 071; 194; and 295) had pour densities between 0.7 to 0.9 g/cm^3 and were pressed into the cans to an approximate density of 2.5 g/cm^3. The 446 material had a much higher pour density of 1.77 g/cm^3. Shock and vibration tests monitored by gamma transmission measurements showed that this material moved within the can when pressed to an approximate density of 2.5 g/cm^3 and caused an unacceptable reduction of the thickness of the layer at distinct positions within the can. Re-pressing this material to a higher density (3.4 instead of 2.5 g/cm^3) by inserting a 5 mm disk under the plug ensured stability of the material, as gamma transmission measurements later confirmed.

The lips of plug and can were TIG-welded together on a semi-automatic machine that enabled repetitive production of precision welds. Pre-flow of inert gas, initial and final slope of the welding current, pulse operation of the current and turntable speed were programmed for optimal reproducibility.

Numbers were engraved into the top part of the cylindrical wall of the cans as shown in Figure 1.

The numbering system was chosen as follows:

- The reference samples distributed by CBNM and NBS respectively for the 031 material indicate the abundance as "031", and a sequential set number of 001 to 070 for CBNM and 071 to 140 for NBS cans:

  CBNM 031 - 001 to 070
  NBS 031 - 071 to 140

- Reference samples with the same sequential number (013 or 120 in this example) with each of the different abundances, form a set. The empty can, provided in addition, has the corresponding sequential number as shown in the following example:

Example

CBNM Set 013	NBS Set 120
CBNM 031 - 013	NBS 031 - 120
CBNM 071 - 013	NBS 071 - 120
CBNM 194 - 013	NBS 194 - 120
CBNM 295 - 013	NBS 295 - 120
CBNM 446 - 013	NBS 446 - 120
CBNM 013	NBS 120

3.3 Sampling for Verification During the Homogeneity Filling Procedure

About 15 samples (2 to 5 g each) were taken during the filling procedure of each of the U_3O_8 materials at a rate of one per day, i.e., about every tenth can. These samples were used for chemical impurity and moisture determinations as well as for checking isotopic homogeneity (see Section V).

3.4 Ultrasonic Identification System

Special attention was given to the individual ultrasonic identification system for each of the reference samples, as described in (8).

Integrated into the plug were identification sensors which work along the general principle of the ultrasonic signature:

- one ultrasonic transducer uniquely identifies the can and is embodied in the structure thus making tampering difficult (identifier),
- another ultrasonic transducer is glued onto the external cover to verify the integrity of the cover (integrity verifier),
- both ultrasonic sensors are connected to a Lemo plug (see Figure 6a) for easy identity and integrity check by simple electronic connection of an ultrasonic reader. These ultrasonic readers are commercially available.

Recording of the identity can be performed using a Polaroid camera to print the pattern that appears on the screen of the portable ultrasonic reader (see Figure 6b). This pattern of the ultrasonic spectrum is unique to each sample can.

The identifier and integrity verifier will indicate any changes in the pattern of the ultrasonic spectrum generated by any tampering with the can.

The Safeguards Inspectorates of the U.S. Nuclear Regulatory Commission, the International Atomic Energy Agency, and the EURATOM Safeguards Directorate can register the ultrasonic pattern of each seal within a set of reference materials for the purpose of safeguards and materials accountability. In order not to destroy the seals, storage temperatures between -10 °C and +40 °C should be maintained.

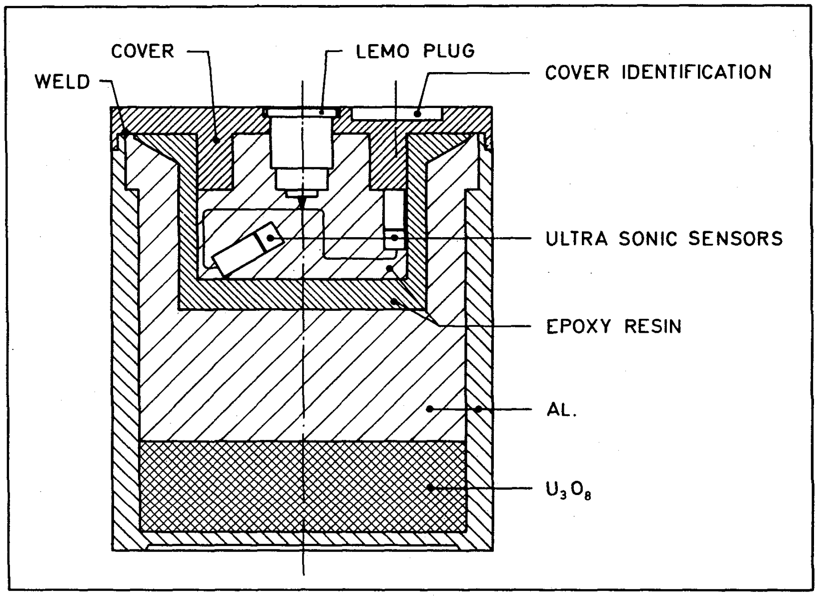


Figure 6a. Ultrasonic Sensors as Integrated Part of Reference Samples

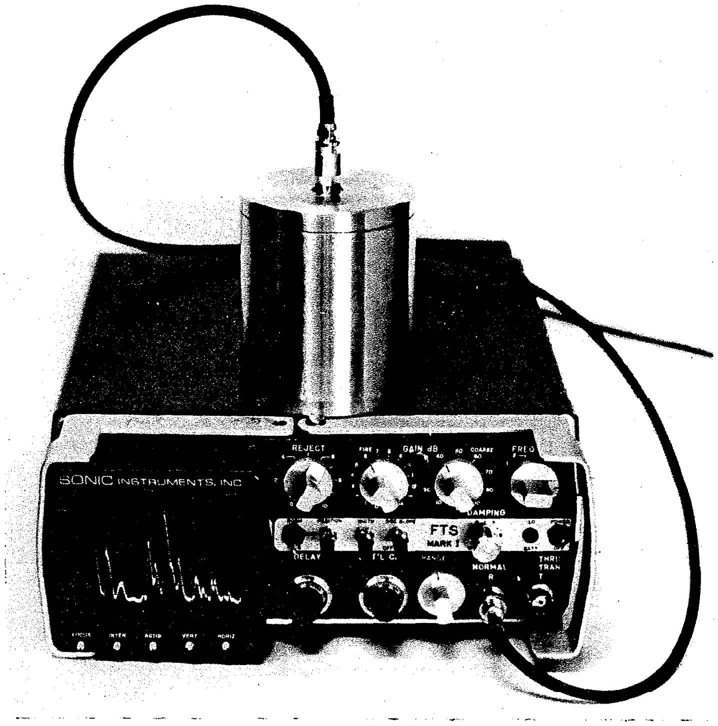


Figure 6b. Registration of the Specific Ultrasonic Pattern of Each Can

Figure 6. Transducer System for the Ultrasonic Identification of the Reference Samples

4. Determination of Properties Relevant for Gamma Measurement

4.1 Chemical Composition and Impurities

Sampling for chemical analyses was done both upon receipt of the material and at the time of canning (see Section III on fabrication).

The uranium oxide was found to contain water and certain other impurities. In addition, the oxygen-to-uranium ratio measurements performed by the supplier (British Nuclear Fuels, Springfields, United Kingdom) indicated a slight excess of oxygen when compared to stoichiometric U_3O_8.

The following measurements were carried out either at CBNM and/or at NBL:

- determination of uranium content
- determination of the impurity content
- determination of the water content.

4.2 Uranium Content Measurements Performed at CBNM

The uranium content of the different batches (Table 1) was calculated on the basis of a calcination of the material at 900 °C. The estimated sum of the total impurities in the form of oxides (see section on Chemical impurities) was subtracted from the mass determined after calcination.

Table 1. Uranium Content at the Time of Packaging

Material	g U/g material
031	0.8456
071	0.8453
194	0.8456
295	0.8452
446	0.8466

The calcination was on 2 to 3 g of material. The U_3O_8 was initially heated in air for 2 hours at 110 °C and then heated in air for 15 hours at 900 °C. From each batch, three samples of the material were taken upon receipt, and three random samples were taken during the filling of the cans. No significant differences between the two sets of analyses were observed, so an average of the six measurements was made. Taking into account the uncertainty of the mass determinations and the evaluation of the total impurities, the maximum uncertainty (95% confidence level) of the elemental content is estimated to be ± 1500 μg/g of material as received.

4.3 Uranium Content Measurements Performed at NBL

Four platinum dishes (75 mL) were cleaned, hot-acid washed, ignited in a furnace at 800 °C for one hour, cooled in a desiccator and weighed. The material in each container (21 g) was then poured into a platinum dish and the dish was reweighed. A special weighing procedure was instituted due to the instability of each material mass. Since the material proceeded to decrease in weight during successive weighings, each set of weighings was plotted and the mass for time "zero" (material as received) was obtained by extrapolation.

To determine moisture content, the samples were dried at 110 °C for two hours, cooled and weighed. Next, the samples were placed in a furnace at 800 °C for two hours, cooled and weighed. The samples were reignited at 800 °C for an additional hour, cooled and weighed again. A weighing procedure similar to the above was necessary in each case.

To ensure constant weight during aliquanting, samples were allowed to equilibrate with room air until the masses were constant. Aliquants were then weighed into beakers and the masses corrected back to ignited masses. Four aliquants from each sample were placed in beakers for isotopic analysis and chemical assay.

The chemical assay aliquants were dissolved in phosphoric acid and titrated using the NBL High Precision Method (9). Aliquants of NBS 950b SRM were ignited at 800 °C for one hour and assayed as control standards. The uranium content and material weight loss determined by NBL is given in Tables 2 and 3.

Table 2. Uranium Content Determinations by NBL[1]
(After Drying and Ignition)

Material	Uranium Content (g U/g)	n
031	0.847685 ± 0.000027[2]	5
071	0.847688 ± 0.000054	5
194	0.847800 ± 0.000083	5
295	0.847758 ± 0.000112	5
446	0.847488 ± 0.000020	5
SRM 950b	0.847783 ± 0.000072[3]	15
	0.847737 ± 0.000038[3]	8

---

[1] Dried, ignited at 800 °C, corrected for isotopic composition
[2] Uncertainities are 1s for n determinations
[3] Certified values = 99.968 ± 0.020% U_3O_8 (0.847731 g U/g)

Table 3. Total Weight Loss Determinations of NBL

Material	Amount Lost (µg/g)
031	1800
071	2300
194	1800
295	2200
446	600

Table 4 gives the values obtained from NBL on the uranium content per gram of material as received. These values are directly comparable to the data presented by CBNM (Table 1).

Table 4. Uranium Content Per Gram of Material (as Received)

Material	Uranium content (g U/g)
031	0.8462
071	0.8458
194	0.8463
295	0.8459
446	0.8470

4.4 Chemical Impurities

The impurity contents of the different batches were calculated using data from spark source mass spectrometry (SSMS) and emission spectrometry analyses performed by the Studiecentrum voor Kernenergie/Centre d'Etude de l'Energie Nucleaire (SCK/CEN), Mol, Belgium.

A panoramic analysis, covering 72 elements of each base material was done by SSMS. Two samples taken during the canning of each material were analyzed by emission spectrography. Thirty two elements were rechecked. The results of the SSMS analyses indicated that no contamination occurred during the preparation step.

The maximum impurity content has been estimated by summing the measured concentrations and the detection limits for a number of elements (see Table 5).

Table 5. Impurity Content

Material	Sum of Impurities $Z \leq 30$ (μg/g)	Sum of Impurities $Z \geq 30$ (μg/g)
031	< 500	< 6
071	< 300	< 6
194	< 400	< 6
295	< 200	< 6
446	< 1000	< 10

The following elements were detected.

$Z \leq 30$	Li	Be	B	F	Na	Mg	Al	Si	P	S	Cl	K
	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
$Z \geq 30$	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ru
	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Cs	Ba	La
	Ce	Pt	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	Hf	Ta	W	Re	Os	Ir	Au	Hg	Tl	Pb	Bi	Th

4.5 Determination of the Water Content

The moisture content of the material sampled at the time of canning was determined by heating the material to 300 °C under dry nitrogen and measuring the liberated water by Karl Fischer titration. Three samplings per batch were taken during the filling of the cans and four analyses per sample were performed (Table 6). The uncertainty on these determinations does not exceed ± 150 $\mu g/g$ of material.

Table 6. Moisture Content

Material	μg H_2O/g Material
031	2525
071	3038
194	2314
295	3000
446	822

4.6 Estimation of the Light Element Content

The weight losses observed during calcination consisted of water, oxygen, and a negligible amount of volatile substances. After rounding off and taking a large uncertainty for the small contributions of volatile substances and hyperstoichiometry, a conservative estimate of the maximum content of light element impurities in the material is presented in Table 7.

Table 7. Maximum Content of Impurities $Z \leq 30$ in U_3O_8

Material	Impurities $Z < 30$ ($\mu g/g$ material)
031	$\leq$ 4100
071	$\leq$ 4600
194	$\leq$ 4000
295	$\leq$ 5000
446	$\leq$ 2500

4.7 Estimation of the Heavy Element Content

The content of elements with $Z>30$ in the different materials does not exceed 10 $\mu g/g$ (see Table 5).

4.8 Radioactive Impurities

The occurrence of spurious gamma-lines (other than from ^{238}U daughters) was tested on one reference sample per abundance by looking for other more intense gamma lines of ^{232}U, ^{233}U, ^{237}U, and their respective daughters. NBS and CBNM used their respective gamma-counting system for all gamma spectrometry measurements, including determining the radioactive impurities (Figure 2a for CBNM and Figure 2b for NBS).

4.8.1 ^{232}U and Daughter Products-CBNM Measurements

It was essential to determine the ^{232}U impurity content of the materials because spurious gamma-lines of ^{232}U daughter products exist in the energy range used by low resolution NaI(Tl) gamma spectrometers for ^{235}U abundance measurements.

The major effect is caused by the gamma-line of ^{212}Pb at 238.5 keV belonging to an energy range used for background subtraction when measuring the 185.7 keV gamma-line.

Test results in Table 8 show that the ^{232}U impurities of the materials are small enough to allow the use of the reference samples with NaI detectors. However, the counting ratio (238.5/185.7) for the 031 material will grow from 0.006 in 1982 (three years after chemical separation) to about 0.01 in 1989 and introduce a significant bias effect.

Table 8. ^{232}U Content as Determined from the Gamma Peak Rate of the ^{212}Pb Daughter at 238.5 keV Relative to ^{235}U at 185.7 keV

Material	Gamma Peak Ratio (238.5)/(185.7) $\times 10^2$	Isotope Ratio ^{232}U/^{235}U $\times 10^9$
031	0.62	0.8
071	$\leq$ 0.02[2]	< 0.03
194	0.03	0.03
295	0.01	0.01
446	0.08	0.1

---

[1] Date measured 1982

[2] Detection level for 238.5 keV gamma-line measurement

4.8.2 ^{233}U, ^{237}U and Daughter Products-CBNM Measurements

Spurious gamma-lines which might bias low resolution gamma measurements of the ^{235}U abundance, are known for ^{233}U and for ^{237}Np from the fast decay of ^{237}U after chemical separation. Tests for identifying such impurities were performed by looking for the lines of ^{237}Np at 212 keV and of ^{233}Pa at 312 keV (^{233}Pa is a daughter product of ^{237}Np) as well as for the most intense lines of ^{233}U at 164.6 keV and 245 keV. Neither impurity was detected, with detection limits of ^{233}U/^{235}U $\leq 5\times10^{-5}$ and ^{237}Np/^{235}U $< 1\times10^{-6}$. As a result, bias effects, if any, are smaller than 0.05%.

4.9 U_3O_8 Surface Sample Density

The infinite thickness performance of the U_3O_8 reference samples was tested in order to ensure that the counting rate from the ^{235}U gamma-radiation at 185.7 keV will correspond to $\geq$ 99.9% of the radiation from an infinitely thick U_3O_8 layer.

For that purpose the following measurements were performed:

- the gamma-counting rate of ^{235}U at 185.7 keV as a function of the thickness of a U_3O_8 layer, with different collimators (viewing angles)
- the uniformity of the U_3O_8 surface density of the reference samples by gamma-transmission measurements.

4.9.1 Gamma-Counting Rate Versus U_3O_8 Layer Thickness

Additional U_3O_8 samples identical to the reference samples, were prepared to test the degree of infinite sample thickness for gamma-radiation at 185.7 keV. These samples contained uranium oxide ranging from 100 to 220 grams, equivalent to area sample densities (m_s) from 2.6 to 5.7 g/cm^2 at a sample diameter of 7.0 cm. Samples were made from the 446 material.

Measurements were performed with the gamma measurement equipment as shown in Figure 2a. Different collimator dimensions were chosen, corresponding to length/diameter ratios (l/d) of 2.0, 1.33 and 0.50, to measure the variation of the gamma-counting rates relative to the counting rate of a reference sample (m_{so} = 5.2 g/cm^2) with the same ^{235}U abundance (see Figure 7).

For comparison, the counting rate variation (dCp) for the 185.7 keV gamma-radiation perpendicular to sample surface was calculated:

$$dCp/Cp = [(\exp{-m_s u_s})-(\exp{-m_{so} u_s})]/[\exp{-m_{so} u_s}] \quad (3)$$

m_{so} = surface density of reference samples, m_{so} = 5.2 g/cm2
m_s = surface density of samples with variable thickness
u_s = attenuation coefficient of U_3O_8.

Figure 7 shows that the measured variations approach the curve dCp/Cp calculated with an attenuation coefficient of U_3O_8, u_s = 1.2 cm^2/g when the solid angle for the gamma radiation decreases (increasing ratio of collimator length, l, to diameter, d. A comparison of the observed to the calculated dC/C value indicates that samples with a density of 5.2 g/cm^2 have a minimum value of 99.86% of infinite thickness.

4.9.2 Uniformity of the U_3O_8 Area Density of the Material

Gamma-transmission measurements were made on the pressed uranium oxide powder layers within the Al cans. These measurements were performed at the center of the sample surface and at 9 areas distributed over the sample surface, for 8 samples of each of the 5 reference materials used (Figure 8).

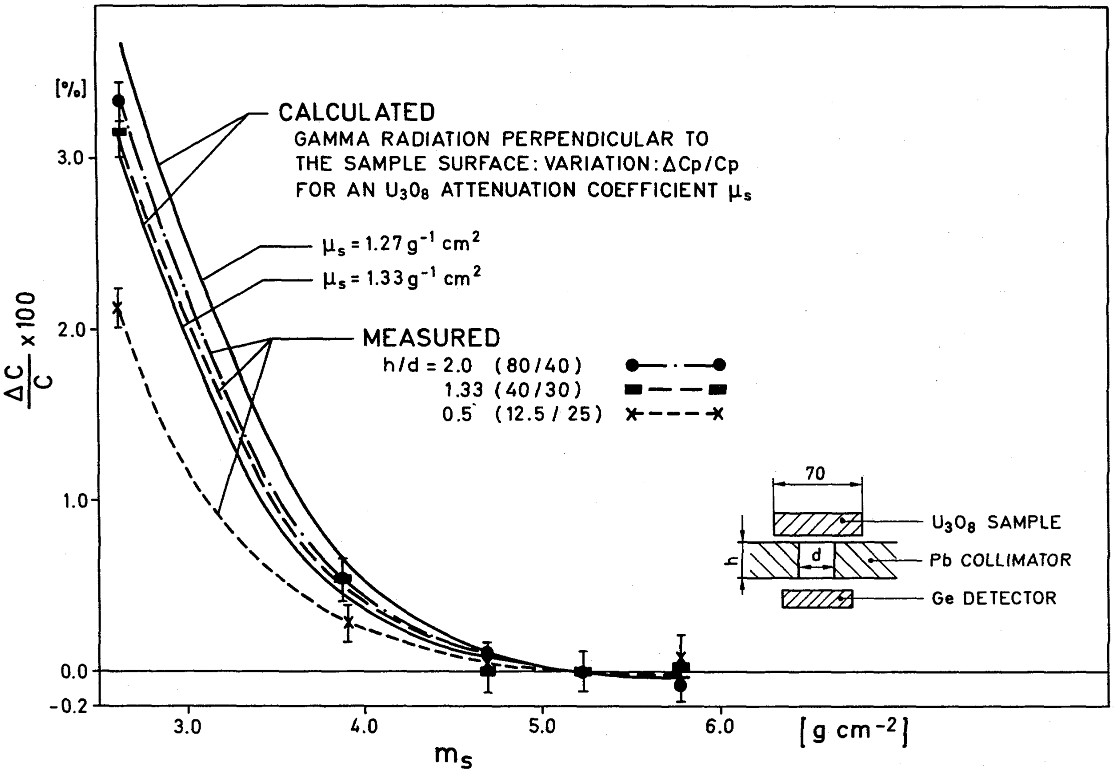


Figure 7. Variation of Counting Rate $(\Delta C/C)$ of U_3O_8 Samples versus Areal Density (m_s) Relative to a Reference Sample (m_{so})

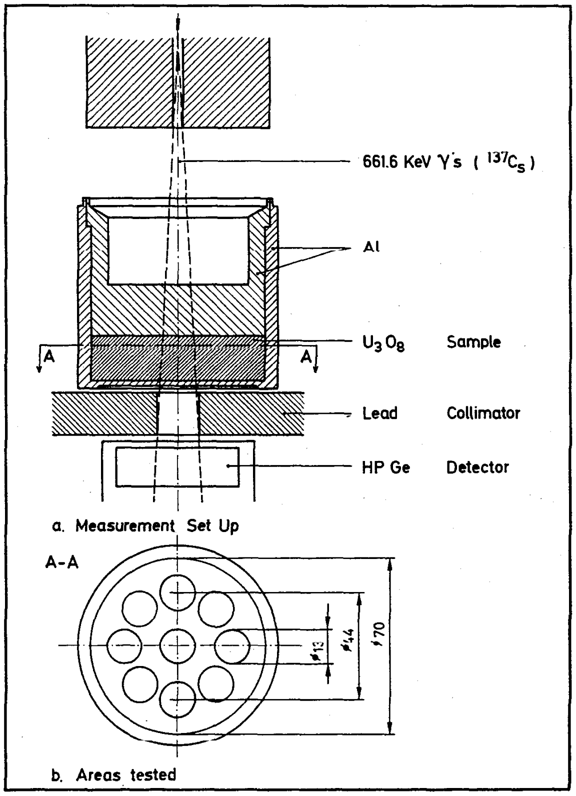


Figure 8. Set-up for U_3O_8 Mass Distribution Uniformity Tests by Gamma Transmission Measurements

The transmission tests were conducted with a collimated ^{137}Cs gamma-beam for the determination of the fluctuations of the counting rate of the transmitted gamma-line at 661.6 keV. These fluctuations are a measure of the non-uniformity of the uranium oxide sample mass perpendicular to the sample surface. The measurements were calibrated with "well defined" uranium oxide layers. An Al absorber was used as a reference for testing the stability of the measured gamma-line counting rate.

The following results have been obtained for the fluctuations (dm_s) of the sample surface density around the mean value of 5.20 g/cm^2.

Material batch	031	071	194	295	446
Fluctuations dm_s[g/cm]	$\leq \pm$ 0.15			$\leq \pm$ 0.25	

Conclusions

It can be concluded that the ^{235}U counting rate of the reference samples at 185.7 keV will be about 0.10 $\pm$0.06% less than for corresponding (theoretical) samples of infinite thickness. It has been shown that this value is not only influenced by the fluctuations of the uranium oxide surface density but also by the collimator chosen.

4.10 Can Window Thickness

In order that the window thickness uniformity of the cans meets the close tolerances specified in Figure 9, ultrasonic thickness measurements were performed on all of the cans using a thickness reference window. This reference window was specially prepared from the same Al-alloy 6061-T6 base material stock used in the manufacturing the reference material cans.

Thickness values on this reference window were determined at four "well defined" measuring locations by means of a comparator gauge (precision achieved: ±1 μm) which was calibrated with gauge blocks according to DIN 861 and NFE 11010 specifications (maximum deviation of nominal thickness ± 0.10 μm). The surface of each calibrated location on the reference window is identical to the surface of each location involved in an ultrasonic determination. The ultrasonic meter was recalibrated at frequent intervals in the course of a day's operation in order to minimize errors caused by instrument drift. Under these conditions an accuracy of ± 5 μm on the window thickness determinations was achieved.

The cans were selected in sets of 6 (5 reference samples and 1 empty can) in such a way that the maximum difference of the mean window thickness: $\bar{x}_{13}$ between any two cans in each set is 0.015 mm (see Figure 9).

An example of can window thickness measurements, as provided with each container, is given in Figure 5.

The window flatness was better than 0.1 mm for all fabricated reference samples as measured with a precision dial indicator along 4 diameters of each window.

1) $1.980 \text{ mm} < \bar{x}_{13}, \bar{x}_8, \bar{x}_5, \bar{x}_4, \text{ and } x_{centr.} < 2.020 \text{ mm}$

2) $s_{13} < 0.015 \text{ mm}$

$s_8, s_5, s_4 < 0.010 \text{ mm}$

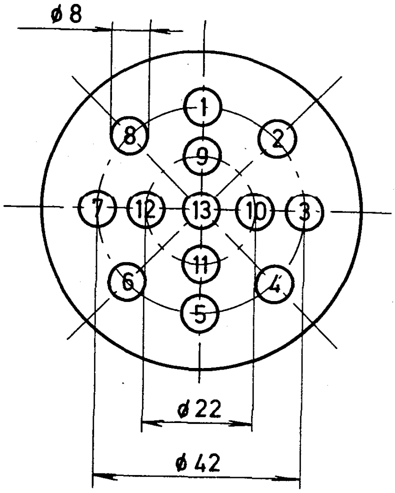
3) For each can $| \bar{x}_8 - \bar{x}_4 | < 0.005 \text{ mm}$

4) For each set of 6 cans (5 abundances + 1 empty can)

$(\bar{x}_5)_{max} - (\bar{x}_5)_{min} < 0.010 \text{ mm}$

and

$(\bar{x}_{13})_{max} - (\bar{x}_{13})_{min} < 0.015 \text{ mm}$



$\bar{x}_{13}$: mean thickness all points 1 to 13
$\bar{x}_8$: mean thickness points 1 to 8
$\bar{x}_5$: mean thickness points 9 to 13
$\bar{x}_4$: mean thickness points 9 to 12
xc : thickness control points 13
s_5 : standard deviation on a single measurement for 5 control points
s_4 : standard deviation on a single measurement for 4 control points
s_{13} : standard deviation on a single measurement for all points

Figure 9. Specification for Uniformity of Window Thickness

4.11 Evaluation of the Uncertainty Contributions of a ^{235}U Abundance Determination by Gamma Counting at CBNM

All uncertainty contributions specified in the following sections correspond to a confidence level of $\geq$ 95%.

4.11.1 ^{235}U Abundance of Reference Samples

The stated uncertainties for the ^{235}U isotope abundances as determined by mass spectrometry, dA_r/A_r, are summarized in Table 9. The values given contribute directly to the uncertainty of the ^{235}U abundance determination by gamma counting, whereas the maximum uncertainty on the isotopic inhomogeneities, dA_h/A_r, will be smaller, dependent on the material distribution within the reference samples.

Table 9. Uncertainties of ^{235}U Abundances from UF_6 Mass Spectrometry (CBNM)

Material	031	071	194	295	446
$\pm dA_r/A_r$ 100(%)	0.07	0.07	0.07	0.07	0.07
$\pm dA_h/A_r$ 100(%)	0.023	0.013	0.014	0.006	0.012

4.11.2 Chemical and Physical Sample Properties

Properties of the reference samples which influence the overall uncertainty of an abundance measurement by gamma-counting were described earlier in this chapter. The effect of properties other than the ^{235}U abundance on the measurement of the ^{235}U gamma radiation at 185.7 keV corresponds to uncertainties (dK/K) of the correction factors, K, in equation (1) of section I.

A. Chemical Properties

Measurements on all five material batches and on several samples per batch as described in this section, have shown the maximum impurity content to be as follows:

$Z \leq 30$: $\leq$ 5000 $\mu g/g$
$Z > 30$: $\leq$ 10 $\mu g/g$

This corresponds to a gamma attenuation with an uncertainty of:

$$(dK_m/K_m) x100 \leq - 0.051 \%.$$

The major contribution to the above value results from the water content of the materials ($\leq$ 3200 $\mu g/g$ U_3O_8).

B. Physical Properties of the Samples

The uncertainty of the U_3O_8 surface density and can window thickness are described below:

- U_3O_8 surface density: the residual inhomogeneity of the U_3O_8 surface density measured over the sample surface, perpendicular to the can window, is < ± 5% for a mean surface density of 5.2 g/cm^2. This corresponds to an uncertainty of:

$$(dK_s/K_s)x100 < \pm 0.07 \%.$$

- Aluminum can window thickness: an uncertainty of the effective can window thickness of < ± 0.015 mm within a set of reference samples will introduce an uncertainty of the measured counting rate of:

$$(dK_c/K_c)x100 < \pm 0.10 \%.$$

In both cases the uncertainties are typical for the viewing angles encountered in detector/collimator configurations corresponding to collimator height to diameter ratios (h/d) to 0.3 (5).

4.11.3 Overall Gamma-Counting Uncertainty of Reference Samples

The gamma counting uncertainty contributions from reference sample properties, outlined in the previous section, are maximum values. They are independent in origin and can be used as a means of calculating the maximum overall gamma emission rate non-uniformity at 185.7 keV of the reference samples from a given batch of material, via the following equation:

$$dC/C(\text{calculated}) \leq [\ (dA_H/A_R)^2 + \sum_K (dK/K)^2\ ]^{1/2} \qquad (4a)$$

with $(dA_H/A_R) \lessdot \pm 0.023 \%$ and the quadratic summation of the maximum uncertainties for the correction factor, K,

$$\Sigma\ (dK/K)^2 \quad = (dK_m/K_m)^2 + (dK_s/K_s)^2 + (dK_c/K_c)^2 \qquad (4b)$$

(see Equation 1), using the values: $dK_m/K_m < 0.051\%$, $dK_s/K_s < 0.07\%$, and $dK_c/K_c < 0.10\%$ it follows for the maximum overall gamma counting uncertainty of samples with the same ^{235}U abundance:

$$(dC/C)\cdot 100\ (\text{calculated}) < \pm\ [(0.023)^2+(0.051)^2+(0.07)^2+(0.10)^2]^{1/2}\%$$

$$(dC/C)\cdot 100\ (\text{calculated}) < \pm\ 0.14\%.$$

This value is practically unaffected by dA_H/A_R and is in good agreement with results given by the CBNM Gamma Spectrometry Section.

The overall uncertainty of the reference samples for the calibration of abundance measurements by gamma spectrometry can be derived from:

$$dC/C\ (\text{overall}) = [(dA_R/A)^2 + (dC/C)^2\ (\text{calculated})]^{1/2}.$$

With the maximum value of $dA_R/A_R = \pm\ 0.07\%$ in Table 9 it follows:

$(dC/C) \cdot 100(\text{overall}) < \pm\ [(0.07)^2+(0.023)^2+(0.051)^2+(0.07)^2+(0.10)^2]^{1/2}$

$(dC/C) \cdot 100(\text{overall}) < \pm\ 0.16\%$.

This is a maximum value which will reduce to < 0.14% for samples belonging to the same set because of the smaller tolerance of the can window thickness (± 0.015 mm within a set compared to ± 0.020 mm, and $dK_c/K_c < 0.07$ instead of <0.10).

5. ^{235}U/U Characterization

The ^{235}U/U abundances were obtained as

$$^{235}\mathrm{U/U} = \frac{^{235}\mathrm{U}/^{238}\mathrm{U}}{^{234}\mathrm{U}/^{238}\mathrm{U} + {}^{235}\mathrm{U}/^{238}\mathrm{U} + {}^{236}\mathrm{U}/^{238}\mathrm{U} + 1} \qquad (5a)$$

The ^{235}U/^{238}U ratios were characterized by two different isotope mass spectrometric techniques:

a) Thermal ionization mass spectrometry (ThIMS)- where a sample is thermally ionized and the ratios of the ion beam intensities of all isotopes are measured by scanning the ion beams over a single collector. The ^{235}U/^{238}U ratios are calculated from measured ratios:

$$(^{235}\mathrm{U}/^{238}\mathrm{U})_{\text{material batch}} = K_{5/8} \times (^{235}\mathrm{U}/^{238}\mathrm{U})_{\text{measured}} \qquad (5b)$$

where K is a correction factor for systematic errors and 5/8 denotes ^{235}U/^{238}U.

b) Uranium hexafluoride mass spectrometry (UF$_6$MS)- where the ^{235}U and ^{238}U ion beams are collected simultaneously in two different collectors of a mass spectrometer equipped with a permanent magnetic field and working with a constant accelerating voltage. In the measurement circuitry the ratio of ion currents of the unknown is converted to a ratio of voltages and is compared to the same ratio of a reference sample (in this case: a synthetic isotope mixture). This yields a correction factor directly expressed as an α-value. Hence, the α-values obtained

$$(^{235}\mathrm{U}/^{238}\mathrm{U})_{\text{material batch}} = \alpha \cdot (^{235}\mathrm{U}/^{238}\mathrm{U})_{\text{synthetic mixture}} \qquad (5c)$$

through UF$_6$ mass spectrometry have better reproducibility than ThIMS. If these measurements can be performed directly against accurate synthetic isotope mixtures, they have the potential for better accuracy.

The ^{234}U/^{238}U and ^{236}U/^{238}U ratios were obtained only from ThIMS.

5.1 Measurements Made at CBNM by Mass Spectrometry

All measurements were carried out after all precautions had been taken to correct or eliminate known systematic errors. Correction for additional systematic errors, including mass discrimination in the ion sources, were considered separately for ThIMS and UF$_6$MS.

5.1.1 Thermal Ionization Mass Spectrometry

Correction from unknown sources of systematic error, including the isotope fractionation in the ThIMS ion source (the most difficult but also the most important error), were determined by measuring synthetic mixtures of enriched ^{235}U and ^{238}U isotopes, calculated from their preparation to be accurate to ± 0.01 %. Measuring the mixtures in the mass spectrometer, and correcting these measurements for all known errors yielded "observed" values R_{obs} for these ratios. The difference between "prepared" and "observed" ratios for the mixtures permitted the detection, quantification, and correction for isotope fractionation by means of the correction factor $K = R_{prep}/R_{obs}$.

The accuracy of the $^{235}U/^{238}U$ characterization was then determined by the precision of the K-factor and the accuracy of the isotope mixtures.

The mixtures were made over a range of $^{235}U/^{238}U$ ratios that bracketed the samples (see Table 10) and demonstrated that:

a) the measurement procedures and instrumentation used were linearly responding to ion beams to the precision indicated

b) the isotope fractionation observed was independent of isotope abundance or ratio and only dependent on isotope mass

c) a reading or transcription error in the preparation of any single mixture had not occurred

d) a weighing error in the preparation on any single mixture was not detected.

This approach has been used previously to produce Isotopic Reference Materials for boron (13) and lithium (14,15).

Since isotope fractionation, as determined over a span of 3 mass units difference (235-238), was only 0.03%, or 0.01% per mass unit, a linear extrapolation could be made to the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratio measurements of 0.04% and 0.02% respectively.

5.1.2 UF_6 Mass Spectrometry

Remaining systematic errors as well as mass discrimination in the UF_6 ion source were cancelled out by measuring directly against synthetic mixtures of enriched ^{235}U and ^{238}U. These mixes were known from their preparation to 0.01% and simulated the isotope composition of the material batches (i.e., the candidate RM's) to within 1%.

The chemical conversion of the mixtures to UF_6 normally requires 2-3 g of material per sample. It was obviously impossible to consume that large an amount of enriched isotopes, therefore, the entire procedure was miniaturized until chemical conversions on a 100 mg scale could be achieved without loss of accuracy (10,18).

The accuracy of the $^{235}U/^{238}U$ characterizations was then determined from the precision of the α-value and the accuracy of the isotope mixtures.

The working scheme followed by CBNM is illustrated schematically in Figure 10.

The various stages are described below:

- preparation of the synthetic mixtures and determination of their uncertainty components

- mass spectrometric measurements and their calibration

- computation the $^{235}U/U$ abundances and their uncertainties.

In each step of the characterization process of the $^{235}U/U$ abundances, the significant systematic errors were quantified, the measurement in that particular step was corrected, the uncertainty of the correction factor(s) was incorporated and the combined uncertainty was transferred to the next step of the process. All uncertainties are be expressed as 2s, this corresponding to a confidence level of about 95%. Propagation of this uncertainty has been done on the basis of the square root of the sum of squares (independent determinations) except when otherwise indicated. This was the case when calculating the uncertainty on $^{235}U/U$ abundances (Equation 8).

5.1.3 Preparation of Synthetic Uranium Isotope Mixtures

Enriched isotopes were purified chemically and converted to the highly stable U_3O_8. On a weight basis they were mixed to achieve different ratio values (see Table 10) in the range 0.003-0.05 corresponding to $^{235}U/U$ abundances of 0.003-0.045 (or 0.3-4.5 mass %).

The important steps in the preparation of the mixtures were:

- determination of the isotopic purity of the highly enriched isotopes

- determination of the chemical purity of the enriched isotope

- weighing of the enriched isotope oxide fractions and corrections for water uptake

- dissolution of the weighed fractions.

5.1.4 Isotopic Purity of the Highly Enriched Isotopes

The isotopic purity of the isotopes used for the synthetic mixtures was accurately determined through isotope dilution mass spectrometry. The results of these measurements are listed in Table 11.

The wide dynamic range encountered in the isotope ratios of the materials made it necessary to determine some of the small abundances by comparing them with a known amount of ^{233}U added as an "internal isotopic standard" (see the upper part of Figure 10).

The accuracy of the $^{235}U/^{238}U$ ratios in the mixtures is dominated by the accuracy of the ^{235}U abundance in the ^{238}U enriched material (16). This material was spiked with IRM 040-1 (^{233}U) (17) to give a $^{235}U/^{233}U$ ratio approximately equal to one and this ratio was measured. The $^{235}U/^{238}U$ ratio was then determined from:

$$^{235}U/^{238}U = {}^{235}U/^{233}U \cdot N_{233}/N_{238}$$

where N_{233} is the number of atoms ^{233}U added. Both N_{233} and N_{238} were determined from weighing the calcined oxide and correcting for oxygen content and isotopic purity.

Table 10. Prepared Isotope Mixtures, with Uuncertainties (2s) and their Components; 100 parts per 10^6 = 0.01%

prepared isotope mixtures		uncertainty (2s) on ratio in mixture: $2s_R/R$ in parts per 10^6	uncertainty components of $2s_R/R$ in parts per 10^6 (2s) from differences in			
Ident. Nos.	^{235}U/^{238}U atom ratio $R_{prep} + 2\ s_R$		isotopic purity	stoichiometry	chemical purity	mass determination
82	0.003 210 19 41	127	113	44	14	34
83	0.003 241 59 41	126	112	44	14	34
84	0.007 238 63 56	78	51	44	14	36
85	0.007 302 88 57	78	51	44	14	36
118	0.007 206 69 61	85	51	44	14	49
119	0.007 326 01 62	84	51	45	14	49
102	0.020 183 6 1 8	91	21	45	14	75
103	0.019 976 7 2 1	103	21	45	14	89
104	0.030 599 0 3 2	105	16	45	14	92
105	0.030 982 0 3 2	105	15	45	14	92
106	0.047 121 6 4 7	101	13	45	14	88
107	0.047 546 7 4 8	100	13	45	14	88

Table 11. Isotope Abundances of Enriched Isotope Material Used to Prepare the set of Synthetic Isotope Mixtures (Uncertainties ±2s).

Isotope Ratios	Enriched ^{235}U	Enriched ^{238}U
$^{233}U/U$	<0.0000002	<0.0000002
$^{234}U/U$	0.0003607 ±0.0000026	0.0000003 ±0.0000002
$^{235}U/U$	0.9994145 ±0.0000060	0.0000234 ±0.0000004
$^{236}U/U$	0.0000953 ±0.0000052	<0.0000001
$^{238}U/U$	0.0001295 ±0.0000015	0.9999763 ±0.0000004

The other minor isotopes were determined in a similar manner. Because of the small ion currents encountered, the measurements were performed using an electron multiplier.

In arriving at the final abundances and uncertainties shown in Table 11 all possible sources of error were considered since the uncertainty of the enriched isotopes is an important component of the total uncertainty of the mixtures. The following sources of error were evaluated:

- Interference from unresolved molecular species: the spectrum was closely examined using the highest sensitivity available since the magnitude of these species depend on the ionizing filament temperature, the latter was lowered until their contributions to the isotope ratios were negligible.

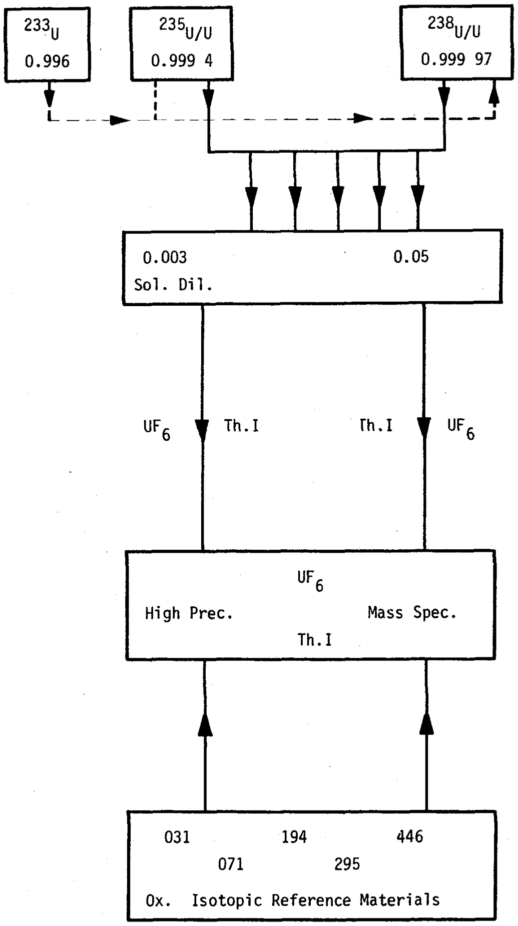
- Uranium blank: the contribution to the uranium mass spectrum from impurity uranium originating from chemical processing was <0.1 ng and from the rhenium filament <0.03 ng. Since 10 μg sized samples were analyzed, errors from this source were negligible.

- The use of an electron multiplier: a knowledge of the isotope discrimination was required. This discrimination was corrected by a factor of 0.23±0.10% per atomic mass unit.

- Time dependent isotope fractionation: the magnitude of this effect was very small. Even so, a correction was made and an uncertainty of ±0.10% per mass unit was assigned to the correction.

- Baseline irregularities: the assumption of a linear trend in the baseline is normally sufficient for estimating the baseline at the position of a peak.

However, for low abundance peaks adjacent to the highly enriched isotopes, more complex corrections were required. The isotope most affected was the



Highly Enriched Isotopes
(Base Materials)

These do not constitute RM's by themselves since they do not bear a certified value which can be used to calibrate a measurement

$^{235}U/^{238}U$

Synthetic Mixtures of
Highly Enriched Isotopes

High Precision Mass Spectrometry

Requires a very high precision in order

- to make full use of the small uncertainty on the isotopic mixtures
- to attain the required uncertainty on the RM batches

Measurement samples must be converted to very pure Uranyl nitrate and UF_6

Isotopic Reference Materials

- Materials to be distributed

Notes:

Ox. = Oxides
Sol.Dil. = Dilution of Solution

Figure 10. Scheme for the Preparation of Synthetic Isotope Mixtures in order to put "absolute" values (with uncertainties) on Isotopic Reference Materials

^{236}U in the ^{235}U enriched material where it was necessary to allow for a 1.5% (1s) uncertainty.

5.1.5 Chemical Purity of the Enriched Isotopes

Enriched isotopes always have a limited chemical purity, but, in this case, similar purities for the two enriched isotope materials were sufficient. Chemical purification of the two enriched isotopes was, therefore, carried out using the same procedure. The isotopes were purified by cation exchange on Dowex 50X8 (100-200 mesh, H-form) resin using a 90% tetrahydrofuran/10% 6M HNO_3 solution as eluent, followed by calcination at 900 °C for 3 hours. The U_3O_8 was redissolved in 6M HNO_3. A second purification step consisted of a peroxide precipitation of the uranium followed by calcination to U_3O_8 at 900 °C for 3 hours.

The chemical purity of the products was about 99.9% before the purification (about 800 μg/g impurities), and 99.99% (about 100 μg/g impurities) after purification (see Table 12).

The purity check was made with the aid of a JEOL-01-BM-2 double focussing spark source mass spectrometer (SSMS). Relative Sensitivity Factors (RSF) were used for the elements detected. Impurity determinations were performed with both Au (99.999%, 200 mesh, Cominco American Inc.) and C (Specpure Graphite, grade I, Johnson Matthey) electrodes. Isotopic compositions of Cl and added spike isotopes ^{86}Sr and ^{88}Sr were used for internal calibration purposes.

Remaining volatile impurities (difficult to determine by SSMS) were eliminated - if present - by calcination for 3 hours at 900 °C.

To account for possible undetected impurities, 200±100 μg/g, instead of 100 μg/g, was added to the total uncertainty of the isotope mixtures. The effect of the purity of the enriched isotopes on the uncertainty of the isotope mixtures is shown in Table 10.

5.1.6 Deviations from Stoichiometry-Water Uptake of the Enriched Isotope Oxides

U_3O_8 was chosen as the chemical form for the enriched isotopes because of its very stable stoichiometry. In this case, an identical composition, not necessarily theoretical (stoichiometric) is needed. U_3O_8 is known to be reproducible to $\leq$ 0.01 % in composition when calcined for a minimum of 1 hour at 900 °C.

Both enriched isotope oxides were calcined simultaneously in quartz tubes for 16 h in a furnace having a temperature uniformity of + 2.5 °C, and a difference between two quartz tubes of 1^{o} maximum at the 900 °C equilibrium situation. This step eliminated volatile impurities.

The calcinations were performed in an air flow of about 7 mL per minute on portions of about 1 g. Subsequently the crucibles were cooled on a large aluminum block and weighed after 24 hours. Another 2-hour calcination followed and the process was repeated until the mass differences were less than 20 μg (error <20ppm) and hence negligible. All operations were performed in a glove-box with a controlled humidity of 10-50 μg water/g dry air. Water uptake was <5 μg on 1-g samples (possible error <5 ppm and hence negligible) during the weighing periods of 1 h maximum. The weighing uncertainty was ≤ 5 μg in all cases.

At this point, samples were taken to determine the isotopic compositions given in Table 11.

5.1.7 Isotope Mixtures and their Uncertainties

A series of synthetic isotope oxide mixtures was prepared by weight, and the abundances were calculated from the preparation ("R_{prep}"). These values are given in Table 10 with their uncertainties, 2s and $2s_R/R$, and with the various components of these uncertainties. Immediately after the weighing, the two isotope oxide fractions were dissolved in 6 M HNO_3. All mass determinations were substitution weighings using calibrated weights against the CBNM standard kilogram. The latter is directly calibrated against the standard kilogram of the Bureau International des Poids et Mesures (BIPM) in Sevres, France.

The $^{235}U/^{238}U$ ratio ($R_{5/8}$) in the mixture was obtained from the $^{235}U/^{238}U$ ratios, (R_A,R_B) in the enriched isotope material, A (enriched "235") and B (enriched "238") as follows:

$$R5/8 = \frac{[R_A(1+ R_B)N_A/N_B + R_B(1+R_A)]}{(1+ R_B)N_A/N_B + (1+ R_A)} \qquad (6)$$

where N is the number of atoms of uranium in the enriched isotope materials. Uncertainties on $R_{5/8}$ were calculated by propagating the errors for all relevant variables in Equation 6 (20). These results are summarized in Table 10.

5.1.8 Mass Spectrometric Measurements and Their Calibration

A. UF_6 Mass Spectrometry

Samples of the material batches and synthetic mixtures following the standard procedure (10). For each isotopic composition, two synthetic mixtures were prepared "bracketing" the nominal value for each material to within 1%. $^{235}U/^{238}U$ values for the material batches were then determined relative to each of the mixtures using Equation 5c. Results are given in Table 13.

B. Thermal Ionization Mass Spectrometry

1. $^{235}U/^{238}U$ Ratio Determinations. Appropriate synthetic mixtures were prepared, measured on the mass spectrometer, and corrected for known instrumental bias, to produce observed values, R_{obs}.

Remaining unknown systematic biases (mostly from isotope fractionation in the ion source) were quantified and an appropriate correction factor, K, was determined, (R_{prep}/R_{obs}). The results are given in Table 14.

Table 12. Spark Source Mass Spectrometric Analysis of the Enriched ^{235}U and ^{238}U Materials

	blanco µg.g^{-1}		^{235}U (µg.g^{-1})				^{238}U (µg.g^{-1})			
element	C	Au	(1) C-matrix	(2) C-matrix	(3) Au-matrix	(4) C-matrix	(1) C-matrix	(2) C-matrix	(3) Au-matrix	(4) C-matrix
B	-	-			0.6					
F	-	-								
Na	-	0.06	20	56	3.7	4	130	47	6.5	8
Mg	-	0.11	< 0.05	0.9	0.05	< 0.05	2.4	1.8	0.6	1.2
Al	-	1.2	3.2	0.6	1.8	0.9	26	0.6	0.8	0.3
Si	1.1	0.54	9.8	6.1	7.5	7	77	14.1	4.6	6.2
P	-	< 0.05	18	6.6	0.8	5	16	3.3	5.6	2.3
S	2.9	0.44	170	17.8	5.1	14	110	12.1	6	10.7
Cl	2.9	3.1	330	30	37	39.3	270	64	67.6	33.8
K	4.5	0.7	1.7	4.7	1.5	6.2	13	7	0.6	8.8
Ca	1.1	0.44	19	1.8	3.2	1.4	9.5	1.5	10.1	1
Sc	-	< 0.4	1.2	1	< 0.4	0.7	1.9	0.7	< 0.4	0.7
Tl	-	< 0.3	51	1.5	< 0.3	0.8	75	1.4	0.5	0.5
V	-	1.1	71	7.6	0.5	3.2	160	8.4	0.8	3.4
Cr	-	0.34	< 0.3	< 0.3	2.1	< 0.3	< 0.3	< 0.3	1.9	1.7
Mn	-	-	< 0.3	< 0.3	< 0.3	0.3	< 0.3	< 0.3	0.6	0.6
Fe	0.7	[15]	41	2.2	16	17.4	27	2.2	[131]	22.1
Co	-	-	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Ni	1.3	-	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Cu	-	-	6.7	1.8	< 0.3	0.5	< 0.3	< 0.3	< 0.3	< 0.3
Sn	-	-	8.4	< 0.6	< 0.6	< 0.6	1.1	1	< 0.6	< 0.6
Zn	-	0.33								
Br	-	0.65								
I	-	0.63								
Σ	~ 15	~ 9	~ 750	~ 145	~ 80	~ 100	~ 920	~ 165	~ 106	~ 100

Note: 40 other elements not detectable(detection limit <<1 µg g^{-1})

(1) before purification (base material, C-matrix)

(2) after ion exchange (base material, C-matrix)

$$2(THFH)^{+}NO_3^{-} + [UO_2(NO_3)_4] \rightleftharpoons (THFH)_2^{+}[UO_2(NO_3)_4]$$

$$+ 2\ NO_3^{-} \xrightarrow{900\ ^\circ C} U_3O_8$$

(3) after peroxide precipitation (Au-matrix)

$$UO_2(NO_3)_2 \text{ sol'n} \xrightarrow[+H_2O_2]{+NH_3(pH2)} UO_4 \xrightarrow{900\ ^\circ C} U_3O_8$$

(4) after peroxide precipitation (C-matrix)

Table 13. Determination of $^{235}U/^{238}U$ Ratios Against Synthetic Isotope Mixtures by UF_6 Mass Spectrometry. Uncertainties Indicated Under the Values are 2s. The Last Column Contains the Results of the "Double Standard" Method, i.e., an Interpolation of the Measurement Between the Two Measurements Against the Two Synthetic Mixtures

Material	Synthetic Mixture Used sample number	 preparation value	UF_6 α-value	"absolute" $^{235}U/^{238}U$ value of material "single standard"	 "double standard"
031	82	0.00321019 ±0.00000041	1.00171 ±0.00056	0.0032157 ±0.0000019	0.0032157 ±0.0000016
	83	0.00324159 ±0.00000041	0.99213 ±0.00052	0.0032161 ±0.0000017	
071	118	0.00720669 ±0.00000061	1.00775 ±0.00031	0.0072625 _0.0000023	0.0072623 ±0.0000017
	119	0.00732601 ±0.00000062	0.99127 ±0.00031	0.0072620 ±0.0000023	
194	102	0.0201836 ±0.0000018	0.99358 ±0.00024	0.0200540 ±0.0000052	0.0200552 ±0.0000038
	103	0.0199767 ±0.0000021	1.00397 ±0.00024	0.0200559 ±0.0000053	
295	104	0.0305990 ±0.0000032	1.00560 ±0.00021	0.0307704 ±0.0000073	0.0307711 ±0.0000051
	105	0.0309820 ±0.0000032	0.99322 ±0.00020	0.0307720 ±0.0000068	
446	106	0.0471216 ±0.0000047	1.00434 ±0.00021	0.047326 ±0.000011	0.0473248 ±0.0000082
	107	0.0475467 ±0.0000048	0.99530 ±0.00025	0.047323 ±0.000013	

Table 14. ThIMS (1st series) Measurements: Correction Factor, K, Determined with Synthetic Isotope Mixtures Over a Range, $R_{5/8}$, 0.0003 - 0.05. Uncertainties Indicated are 2s

$^{235}U/^{238}U$ Mixtures			correction factor, K
Sample number	$R_{preparation}$	$R_{observed}$	= $\frac{R_{preparation}}{R_{observed}}$
82	0.00321019 ±0.00000041	0.0032133 ±0.0000024	0.9990
83	0.00324159 ±0.00000041	0.0032420 ±0.0000032	0.9999
84	0.00723863 ±0.00000056	0.0072419 ±0.0000054	0.9996
85	0.00730288 ±0.00000057	0.0073068 ±0.0000034	0.9995
102	0.0201836 ±0.0000018	0.020186 ±0.000010	0.9999
103	0.0199767 ±0.0000021	0.019987 ±0.000010	0.9995
104	0.0305990 ±0.0000032	0.030606 ±0.000004	0.9998
105	0.0309820 ±0.0000032	0.030990 ±0.000011	0.9997
106	0.0471216 ±0.0000047	0.047137 ±0.000032	0.9997
107	0.0475467 ±0.0000048	0.047529 ±0.000026	1.0004
			0.9997
			2s – ±0.0007 (n–10)

The resulting correction factor, K, demonstrates that the measurement procedure and instrumentation are under control. No significant contamination, transcription, reading or weighing error occurred in any of the mixture preparations, otherwise they would have shown up as "outliers".

The correction factor, K, for all remaining systematic errors, mainly isotope fractionation is 0.9997 ± 0.0007 (2s, n= 10). This correction factor, K, was applied to all $^{235}U/^{238}U$ thermal ionization measurements shown in Table 15. A correction factor per mass unit was calculated [1 -(1 - 0.9997)/3] and K factors derived for the other ratios:

	K	Isotope effect (%)
for $^{235}U/^{238}U$ (3 mass units)	0.9997	0.03
for $^{234}U/^{238}U$ (4 mass units)	0.9996	0.04
for $^{236}U/^{238}U$ (2 mass units)	0.9998	0.02

Table 15. ThIMS Observed and Corrected $^{235}U/^{238}U$ Ratios Uncertainties Indicated are 2s

Material	$^{235}U/^{238}U$ observed	Correction Factor K	$^{235}U/^{238}U$ corrected
031	0.0032203 ±0.0000040	0.9997 ±0.0007	0.0032193 ±0.0000046
071	0.0072704 ±0.0000057	0.9997 ±0.0007	0.0072682 ±0.0000077
194	0.0209090 ±0.0000016	0.9997 ±0.0007	0.020084 ±0.000021
295	0.030830 ±0.000033	0.9997 ±0.0007	0.030821 ±0.000039
446	0.047405 ±0.000039	0.9997 ±0.0007	0.047391 ±0.000051

The unsatisfactory agreement between the UF_6MS and the ThIMS first series values led to a second series of ThIMS measurements, using the same synthetic isotope mixtures, but a different mass spectrometer and analyst. The resulting K factors are given in Table 16. The observed and corrected $^{235}U/^{238}U$ atom ratios are given in Table 17. In Table 18 all the CBNM mass spectrometry measurements are summarized.

5.1.9 Determination of the Minor Isotope Abundances

These abundances were measured relative to the 235 isotope using an electron multiplier. These were then converted to ratios relative to ^{238}U e.g., $^{234}U/^{235}U \times {}^{235}U/^{238}U = {}^{234}U/^{238}U$.

An upper limit for the abundance of ^{233}U was estimated with a scan of the mass spectrum at high sensitivity. The other isotopes were measured by peak-jumping in a sequence 234, 235, 236, 234 ...... under computer control. The sources of error taken into consideration have already been identified earlier in this section. For this series of measurements, 5-μg samples were used and a slightly higher ionizing filament temperature was employed. This resulted in a smaller value for the isotope fractionation correction applied. Allowance was also made for the time dependence of the correction due to the minor isotopes being measured about 40 minutes after the majors. Results are given in Table 19.

Table 16. ThIMS Measurements- Second Series: Correction Factor, K, Determined with Synthetic Isotope Mixtures Over the range, R, 0.003 - 0.05. Uncertainties Indicated are 2s

$^{235}U/^{238}U$ Mixtures			correction factor, K
Sample No.	$R_{preparation}$	$R_{observed}$	$= \frac{R_{preparation}}{R_{observed}}$
82	0.00321019 ±0.00000041	0.0032156 ±0.0000027	0.99832 (n=5) ±0.00084
85	0.00730288 ±0.00000057	0.0073177 ±0.0000086	0.99797 (n=6) ±0.00112
102	0.0201836 ±0.0000018	0.020217 ±0.000005	0.99832 (n=6) ±0.00039
103	0.0199767 ±0.0000021	0.020011 ±0.000012	0.99832 (n=6) ±0.00039
104	0.0305990 ±0.0000032	0.030638 ±0.000045	0.99875 (n=5) ±0.00096
105	0.0309820 ±0.0000032	0.031020 ±0.000028	0.99875 (n=5) ±0.00096
106	0.0471216 ±0.0000047	0.047219 ±0.000057	0.99788 (n=6) ±0.00080
107	0.0475467 ±0.0000048	0.047650 ±0.000008	0.99788 (n=6) ±0.00080

Table 17. ThIMS Observed and Corrected Atom $^{235}U/^{238}U$ Ratios. Uncertainties Indicated are 2s

Material	$^{235}U/^{238}U$ atom ratios observed	Correction factor, K	$^{235}U/^{238}U$ atom ratios corrected
031	0.0032202 ±0.0000004	0.99832 ±0.00084	0.0032146 ±0.0000049
071	0.007276 ±0.000009	0.99797 ±0.00112	0.0072612 ±0.0000122
194	0.020097 ±0.000012	0.99832 ±0.00039	0.020063 ±0.000015
295	0.030827 ±0.000031	0.99875 ±0.00096	0.030788 ±0.000044
446	0.047434 ±0.000050	0.99788 ±0.00080	0.047333 ±0.000063

5.1.10 Computing $^{235}U/U$ Abundance Values

In Table 18 the $^{235}U/^{238}U$ ratios obtained from UF_6MS and ThIMS are compared. The isotope ratios given in Tables 18 and 19 have been used to derive the $^{235}U/U$ abundances according to Equation 5a and these are given in Table 20. The 2s uncertainties given in Table 20, include those from the mass spectrometric measurements and from the isotope mixture preparation process.

Table 18. $^{235}U/^{238}U$ Atom Ratio Values, in Percent as Determined by ThIMS and UF_6 Mass Spectrometry. Uncertainties Indicated are 2s and do Contain the Uncertainties of the Measurements as well as on the Synthetic Mixtures

Material	$^{235}U/^{238}U$ Atom Ratios			
	UF_6MS	ThIMS (first series)	ThIMS (second series)	ThIMS (average)
031	0.32157 ±0.00016	0.32193 ±0.00046	0.32146 ±0.00049	0.32170 ±0.00048
071	0.72623 ±0.00017	0.72682 ±0.00077	0.72612 ±0.00122	0.72652 ±0.00100
194	2.00552 ±0.00038	2.0084 ±0.0021	2.0063 ±0.0015	2.0074 ±0.0018
295	3.07711 ±0.00051	3.0821 ±0.0039	3.0788 ±0.0044	3.0805 ±0.0042
446	4.73248 ±0.00082	4.7391 ±0.0051	4.7333 ±0.0063	4.7362 ±0.0057

Table 19. $^{234}U/^{238}U$ and $^{236}U/^{238}U$ Ratio Determination by ThIMS. Uncertainties Indicated are 2s,(n=6)

Material	$^{234}U/^{238}U$ atom ratio	$^{236}U/^{238}U$ atom ratio
031	0.0000202 ±0.0000012	0.0001465 ±0.0000086
071	0.0000528 ±0.0000031	<0.0000002
194	0.000176 ±0.000010	0.00000286 ±0.00000053
295	0.000289 ±0.000016	0.0000336 ±0.0000024
446	0.00038 ±0.00002	0.000072 ±0.000004

Table 20. CBNM $^{235}U/U$ Isotope Abundances. Uncertainties Indicated are 2s and Correspond to the 95% Confidence Level

Material	$^{235}U/U$	
	UF_6 atom % abundance	ThIMS atom % abundance
031	0.32049 ±0.00016	0.32061 ±0.00047
071	0.72096 ±0.00017	0.72119 ±0.00098
194	1.96575 ±0.00037	1.96750 ±0.00173
295	2.98432 ±0.00048	2.98746 ±0.00390
446	4.51668 ±0.00075	4.52007 ±0.00519

5.1.11 Computation of $^{234}U/U$, $^{236}U/U$, and $^{238}U/U$ Abundance Values

The $^{234}U/U$, $^{236}U/U$ and $^{238}U/U$ abundances are given in Tables 21 through 23. For the conversion from atom abundance to mass abundance, following atomic masses were used (28):

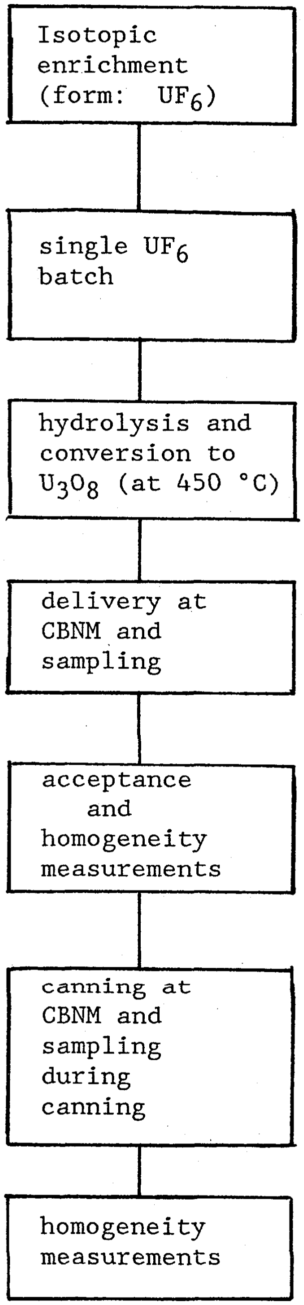
234.0409474 ± 0.0000052
235.0439252 ± 0.0000052
236.0455629 ± 0.0000050
238.0507858 ± 0.0000048

5.1.12 Isotopic Homogeneity

The isotopic homogeneity of the RM batches was verified in several ways:

- the isotopic composition of the samples taken from the batches as delivered (13 samples);
- the isotopic composition of samples taken during the can filling process;
- the agreement of gamma measurements described in Section VI.

The chemical preparation and the sampling procedure of the materials are summarized in Figure 11.



- each batch (expect natural U) was taken from one withdrawal from the enrichment facility
- natural U was directly converted to UF_6

- each batch processed in single lot and stored in a single container except for the 446 material

- each batch was hydrolyzed and converted separately to U_3O_8 as one single lot

- 13 samples were taken from each batch of 30 kg for isotopic homogeneity checks

- relative measurments were performed by UF_6 mass spectrometry on the $^{235}U/^{238}U$ ratio

- during the canning process 1 sample per day was taken (one every 10 cans) yielding about 15 samples per material

- isotopic homogeneity was checked by UF_6 mass spectrometry on the $^{235}U/^{238}U$ ratio and gamma spectrometry on the $^{235}U/U$ ratio

Figure 11. Homogeneity Verification of Materials

Table 21. $^{234}U/U$ Isotope Abundances. Uncertainties Indicated are 2s

Material	$^{234}U/U$ atom abundance	$^{234}U/U$ mass abundance	$^{234}U/U$ uncertainty (2s)
031	0.0000201	0.0000198	0.0000012
071	0.0000524	0.0000515	0.0000030
194	0.0001724	0.0001695	0.0000102
295	0.0002799	0.0002753	0.0000159
446	0.0003636	0.0003576	0.0000208

Table 22. $^{236}U/U$ Isotope Abundances. Uncertainties Indicated are 2s

Material	$^{236}U/U$ atom abundance	$^{236}U/U$ mass abundance	$^{236}U/U$ uncertainty (2s)
031	0.0001460	0.0001448	0.0000090
071	<0.0000002	<0.0000002	-
194	0.0000028	0.0000028	0.0000005
295	0.0000326	0.0000323	0.0000023
446	0.0000687	0.0000682	0.0000042

Table 23. $^{238}U/U$ Isotope Abundances. Uncertainties Indicated are 2s

Material	$^{238}U/U$ atom abundance	$^{238}U/U$ mass abundance	$^{238}U/U$ uncertainty (2s)
031	0.9966290	0.9966709	0.0000091
071	0.9927379	0.9928292	0.0000035
194	0.9801673	0.9804137	0.0000107
295	0.9698443	0.9702149	0.0000165
446	0.9544009	0.9549521	0.0000213

A. Requirements on the Supplier's Chemical Preparation Process

Isotopic homogeneity of four batches of 30 kg U_3O_8 was specified by the requirement that each batch of material had to come from a single UF_6 withdrawal from the isotopic enrichment facility (except, of course, for the natural uranium). Subsequently, each batch was handled as one single lot and was placed in one container to let the UF_6 in the gas/liquid phase homogenize isotopically. Subsequent hydrolysis and calcination to 450 °C was performed in clean installations, one batch at a time, rigorously isolated from any other material (19).

These precautions during the chemical preparation should guarantee isotopic homogeneity at the UF_6 molecular (and hence U atomic) level of the base material for the production of U_3O_8. This requirement was not fulfilled for material 446 which was reported (a long time after delivery) to have been prepared by powder mixing (19).

B. Upon Delivery at CBNM

Each batch was sampled at 12 different positions according to the well-defined scheme given in Figure 12; four samples were taken from the top part, 4 samples from the middle part and 4 from the bottom part of each batch. A 13th sample was taken at random (designated sample "33") and served as the tie-point for the relative measurements. The figures also indicate the sample sizes taken, as well as the identification numbers of all samples in each batch.

A check of isotopic homogeneity was then carried out by UF_6 gas mass spectrometry. After conversion to UF_6 (10), the $^{235}U/^{238}U$ ratio of each sample (1 to 12) was compared to the $^{235}U/^{238}U$ ratio of the 13th sample taken from the same batch (12). Particular attention was given to the UF_6 sample vessels to ensure that there was no cross-contamination (11).

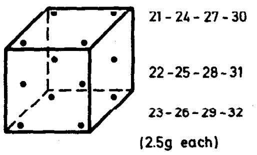
The results of checking the isotopic homogeneity of each material batch on delivery are given in Table 24. These measurements have been considered as acceptance measurements of the material as received and have not been taken into account in the uncertainty of the final values.

Table 24. Check of Isotopic Homogeneity by UF_6 MS of the Base Materials Upon Acceptance. Measurements Performed on 12 Samples Versus a 13th Sample, "33", Taken at Random

Material	$\frac{^{235}U/^{238}U \text{ sample}}{^{235}U/^{238}U \text{ sample "33"}}$	Variability (2s,%)
031	1.00014	0.054
071	0.99988	0.011
194	0.99992	0.018
295	1.00000	0.015
446	0.99998	0.012

1) Samples

Top	Middle	Bottom
21	22	23
24	25	26
27	28	29
30	31	32



Ref. 33: 6g

34 and 35: 20g each

2) Samples taken and distribution CBNM - NBS

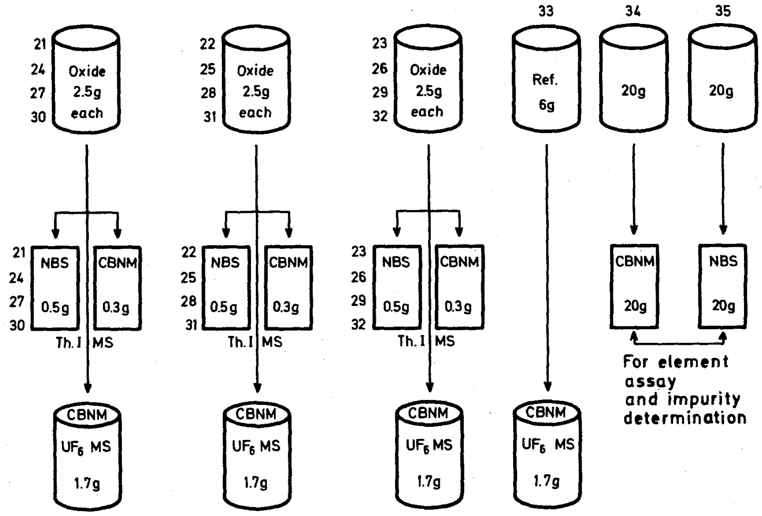


Figure 12. Sampling of U_3O_8 NDA RM 071 Material for Isotopic Measurements

Possible deviations from isotopic homogeneity were observed to be equal to or less than 0.054% (2s) for the 031 material batch and equal to or less than 0.025% for all others on the basis of 1.7 g size samples. The 0.054% uncertainty on the 031 material batch is caused by two of the 12 samples which showed a deviation of about 0.06%in their $^{235}U/^{238}U$ ratios.

5.1.13 Sample Collection During the Filling of the Al Containers

About 15 samples were taken at a rate of one per day i.e., one after each filling of 10 cans. All or part of these samples were analyzed and compared to each other for identity of the $^{235}U/^{238}U$ ratio by UF_6MS. An example is given in Table 25 for one material (the natural uranium, 071).

Table 25. Check of Isotopic Homogeneity by UF_6 Mass Spectrometry During the Filling of the 071 Material, "p" Indicates Samples Taken During the can Filling Process. Uncertainties Indicated are 2s

Sample number	$\frac{235U/^{238}U\ \text{sample}}{235U/^{238}U\ \text{sample "33"}}$	2s
21p*	1.00011	0.00034
22p	0.99996	0.00036
23p	1.00009	0.00037
24p	1.00005	0.00034
25p	1.00004	0.00035
26p	1.00014	0.00035
27p	1.00017	0.00030
28p	1.00008	0.00039
29p	1.00004	0.00034
30p	1.00014	0.00036
31p	1.00011	0.00036
32p	0.99999	0.00034
33p	1.00008	0.00034
34p	1.00002	0.00034
35p	0.99999	0.00034
36p	1.00003	0.00036
37p	1.00011	0.00038
38p	0.99994	0.00046
Average	1.00006	0.00012

Results for all materials are summarized in Table 26. On the basis of 0.5-g samples the isotopic homogeneity of the materials is confirmed to be within 0.025%. The values for the 031 material include one result for one sample which deviated by approximately 0.04% from the others.

5.1.14 Evaluation of the Overall Uncertainty of the $^{235}U/U$ Abundances

For this evaluation, the $^{235}U/U$ in Equation 5a can be written as

$$^{235}U/U = \frac{^{235}U/^{238}U}{^{234}U/^{238}U + ^{235}U/^{238}U + ^{236}U/^{238}U + 1} \qquad (5a)$$

Table 26. UF_6MS Check of Isotopic Homogeneity During Filling of the Cans on the Basis of 0.5 Gram Sample Sizes

Material	$\frac{(^{235}U/^{238}U)\text{ sample}}{(^{235}U/^{238}U)\text{ arbitrary ref.}}$	Variability (2s)
031	1.00024	0.00023 (n=8)
071	1.00006	0.00013 (n=18)
194	1.00006	0.00014 (n=7)
295	1.00005	0.00006 (n=8)
446	1.00001	0.00012 (n=6)

$$A_5 = \frac{R_5}{R_4 + R_5 + R_6 + 1} = \frac{R_5}{N} \qquad (7)$$

where $A_5 = {}^{235}U/U$ and R_4, R_5, and R_6 are $^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$, respectively.

In order to calculate the uncertainty on the abundance A_5, the following quantities are needed: the uncertainties of the three measured ratios, their correlation coefficients and the three partial derivatives of A_5 with respect to these ratios.

The derivation and incorporation of correlation coefficients allows calculation of the 1s-uncertainty on A_5 from Equation 7 as follows:

$$S^2(A_5) = \frac{S_2^2 - 2A_5(\sum_i S_2 S_i P_{2i}) + A_5^2 \sum_{ij} S_i S_i P_{ij}}{(R_4 + R_5 + R_6 + 1)^2} \qquad (8)$$

where $i,j = 1,2,3$ and
$s_1 = s(R_4)$, $s_2 = s(R_5)$, $s_3 = s(R_6)$
$p_{11} = p_{22} = p_{33} = 1$
$p_{12} = p(R_4,R_5)$, $p_{13} = p(R_4,R_6)$, $p_{23} = p(R_5,R_6)$

Using ratios and their 1s-values from Table 19 values for $s(A_5)$ were obtained as given in Table 20.

Terms of p_{ij} when $i \neq j$ were extremely small because at least one factor of the term; either s_i, s_j or p_{ij} was very small. This was due to the fact that $^{235}U/^{238}U$ ratios were measured independently by UF_6MS from the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios by ThIMS.

All components of the overall uncertainty on the $^{235}U/U$ abundances, expressed in parts per 10^6 (2s) of the certified value, are summarized in Table 27.

Table 27. Components of the Uncertainty of the $^{235}U/U$ Abundance Determination and the Verification of Isotopic Homogeneity (Expressed in ppm of Value)

Uncertainty Source	Material				
	031	071	194	295	446
1. Preparation synthetic mixtures					
- isotope purity	113	51	21	16	13
- stoichiometry	44	44	45	45	45
- chemical purity	14	14	14	14	14
- weighing	34	49	89	92	88
2. UF_6MS α-measurements	467	210	160	126	135
3. $^{234}U/^{238}U$ Measurements	1	3	10	16	21
4. $^{236}U/^{238}U$ Measurements	9	<1	<1	2	4
Sub-total	484	227	190	165	170
5. Isotopic homogeneity	230	130	140	60	120
Overall	536	262	236	176	208

5.2 Measurements Made at NBS by Mass Spectrometry

5.2.1 Uranyl Nitrate Dihydrate procedure (Series: 031, 194, 295, and 446)

A. Filament Material

All analyses were performed using a rhenium triple filament ion source (21). Standard high purity rhenium (nominal purity = 99.9%) was used. Different lots of rhenium vary considerably in the observed uranium fractionation pattern and in the amount of UO^+ ion signal generated. Zone- refined rhenium generally produces less UO^+, however it also tends to give a less stable signal with less internal precision than can be obtained with regular rhenium (22). Therefore, zone-refined rhenium is not recommended for this procedure. A U^+/UO^+ ratio of 10^3 or greater after 20 minutes was chosen as a criterion for data collection.

B. Filament Outgassing

The rhenium filaments were outgassed prior to sample loading by heating in a vacuum (less than 2×10^{-5} Pa) and under a potential field of approximately 45V, at a current of 3A through the sample filaments, and 4A through the ionizing filaments, for 1/2 hour. Ideally filaments should be used within 48 hours after removal from the vacuum outgasser to minimize air O_2 absorption.

Most UO^+ during the analysis appears to come from absorbed O_2 on the ionizing filament.

C. Sample Loading

Five microliters of solution containing 1 mg U/mL in 0.8M HNO_3 were loaded onto each of two rhenium sample filaments, and dried as the uranyl nitrate dihydrate for mass spectrometric analysis. Sample sizes from 10 μg U to less than 1 μg U per filament are usable, however since the isotopic fractionation correction is very dependent on sample size (Figure 13), the amount of uranium on the filament had to be very carefully controlled. Drying of the solution onto the filaments was aided by a heat lamp placed above the filaments. Reproducibility of the drying conditions was maintained through the use of a programmable sample dryer (23) which precisely controlled both the current through the filaments, and the drying time. The uranium samples were dried under the following conditions: 40 °C for 10 minutes, 65 °C for 5 minutes, and 100 °C for 1 minute. These drying temperatures correspond to currents through the filaments of 1A, 1.3A and 1.5A at an air flow rate across the filament of 60 meters per minute (200 ft/m). Different air flow rates require readjustment of the filament currents to maintain the proper temperature (Figure 14). It is important that the filament temperature does not exceed 110 °C; at 120 °C the formation of UO_3 may occur which will result in a different isotopic fractionation pattern for those samples that have been partially converted to this oxide.

The first step of the drying procedure deposits the uranium on the rhenium filaments as uranyl nitrate hexahydrate and the second step melts the hexahydrate on the filament to ensure good sample-filament contact (melting point of uranyl nitrate hexahydrate is approximately 60 °C). Thermodynamic data indicates that a relative humidity of at least 44% is needed to ensure melting of the hexahydrate before conversion to the trihydrate (24,25). The final step in the drying procedure converts the hexahydrate, through the trihydrate, to the dihydrate. Samples loaded in this manner have been shown to be stable and give highly precise data for up to one year after being loaded on the filaments. However, the samples probably pick up water of hydration and convert back to the tri- or hexahydrate, thus requiring more pump-down time in the mass spectrometer.

D. Analysis Procedure

After the pressure in the mass spectrometer source had reached 2×10^{-5} Pa, liquid nitrogen was added to the source cold trap to further reduce the pressure to 2×10^{-6} Pa. The ionizing filament was heated to 2140 °C for 5 minutes after which the sample filaments were also turned on with a current of 1.0A through the sample filaments for an additional 5 minutes. After a total time of 10 minutes, the filaments were turned off and the liquid nitrogen was removed from the cold trap. This initial heating step is to remove adsorbed oxygen from the filaments and source parts before the analysis.

After the source pressure had returned to 2×10^{-6} Pa, liquid nitrogen was again added to the source cold trap. The ionizing filament was set at 2140 °C using an optical pyrometer (0.65 μm wavelength, not corrected for emissivity) and the sample filaments were set to a current of 1.50A. At 5 minutes into the analysis the sample filament currents were increased to produce a total uranium

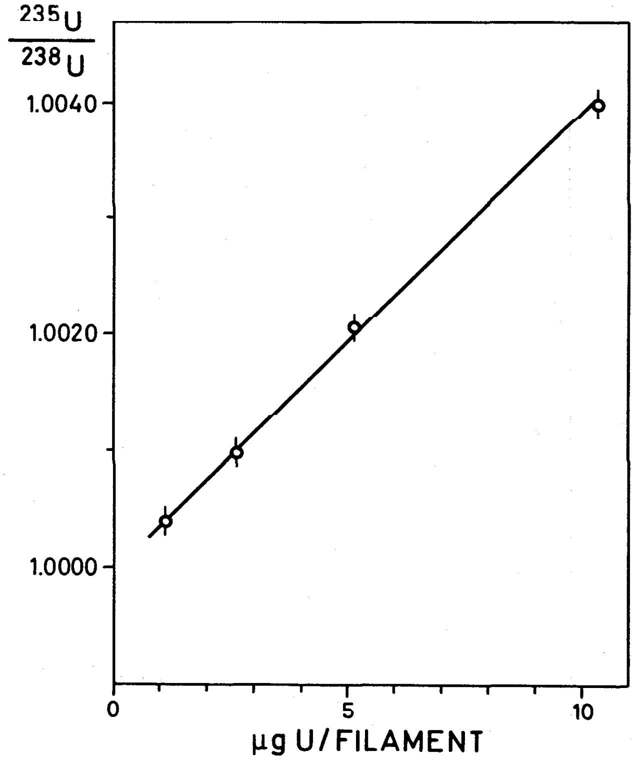


Figure 13. Observed $^{235}U/^{238}U$ Ratio of SRM U-500 versus Sample Size

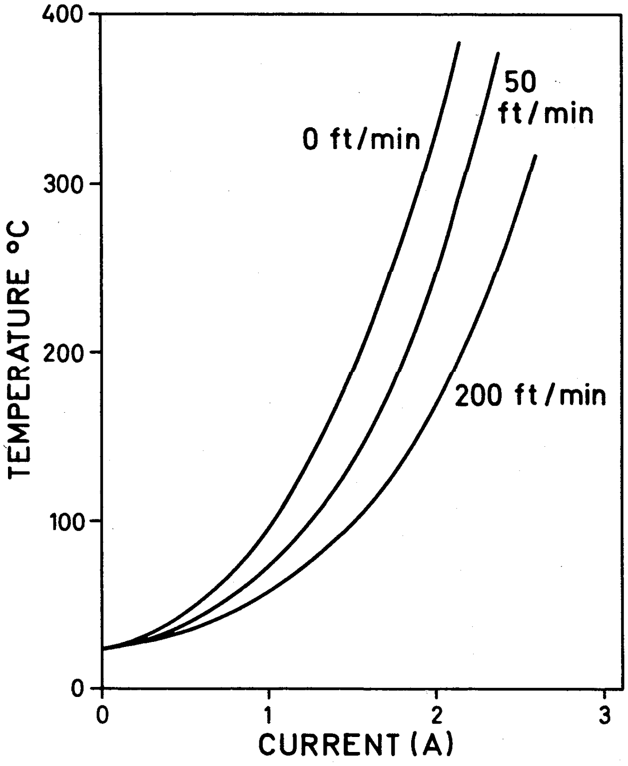


Figure 14. Effect of Air Flow on Rhenium Filament Temperature

ion current at the collector of 2 x 10^{-11}A. The sample filament currents were increased at 10 and 15 minutes into the analysis to produce uranium ion currents of 4 x 10^{-11}A and 6 x 10^{-11}A, respectively. At 20 minutes the ionizing filament temperature was readjusted to 2140 °C and the sample filaments were adjusted, if necessary, to maintain a 6 x 10^{-11}A total uranium signal. After baseline measurements, isotope ratio measurements were made starting at 30 minutes into the analysis.

The $^{238}U/^{235}U$ ratio measurements were made for twenty minutes, after which the sample filaments were increased to obtain a total ion current at the collector of 6 x 10^{-10}A. The increased signal intensity was necessary to measure the minor isotopes. The $^{234}U/^{235}U$ and $^{236}U/^{235}U$ ratios were measured by mass scanning and were bracketed by $^{238}U/^{235}U$ ratio measurements to allow corrections for isotopic fractionation. Observed isotopic ratios were corrected to absolute values by comparison with samples of SRM U-500 analyzed under identical conditions. SRM U-500 has a certified $^{235}U/^{238}U$ ratio of 0.9997.

5.2.2 UO_3 Analysis Procedure (071 series)

Due to the recertification of several uranium isotopic SRM's and a calibrated measurement of the isotopic composition of SRM 960 (currently an assay standard of nominal 0.71% ^{235}U abundance), synthetically prepared calibrated mixes were available for determining the isotopic fractionation corrections for the 071 series material. These calibration mixes were prepared from chemically and isotopically pure ^{238}U and ^{235}U solutions which were assayed prior to mixing using an NBS modification to the NBL High Precision Titrimetric Method which is based on the Davies-Gray technique.

A. Filament Material and Filament Outgassing

These procedures and materials were identical to those used for the uranyl nitrate dihydrate analysis procedure discussed previously.

B. Sample Loading and Analysis Procedure

The major loading and analysis procedures used are discussed in detail in NBS Special Publication 260-27 (27). The same initial drying conditions used for the uranyl nitrate dihydrate procedure were used, followed by heating of the filaments in air to approximately 600 °C for 3 seconds to convert the sample to UO_3. The sample analysis procedure followed the same timing and signal intensity levels as was employed for the uranyl nitrate dihydrate procedure.

5.2.3 Instrumentation

Isotope ratio measurements were made on an NBS designed thermal ionization mass spectrometer with a 30 cm radius of curvature, 90° magnetic sector. The instrument was equipped with a thin lens "Z" focusing ion source, and a multi-component, deep-bucket Faraday cage collector (26). The remainder of the measurement circuitry consisted of a vibrating reed electrometer, voltage-to-frequency converter, scaler, and programmable calculator. Timing, magnetic field switching, and data acquisition were controlled by the programmable calculator.

5.2.4 Sample Dissolution and Preparation of Calibrated Mixes

A sampling scheme to accurately determine the level of enrichment and to demonstrate the degree of homogeneity was designed by the NBS Center for Applied Mathematics and supplied to CBNM for guidance during sampling and packaging of the NDA samples. From the sampling scheme, NBS received twelve 0.5 gram samples from each enrichment for isotopic analysis. An example of the actual sampling locations is given in Figure 12.

Approximately 3mg of U_3O_8 was taken from each of the 12 sample vials for each of the four material lots. The samples were dissolved in 1-2 mL of HNO_3 by heating. The sample solutions were evaporated to dryness and then diluted with 0.8M HNO_3 to give a solution concentration of 1mg U/mL.

The calibration mixes were prepared from ^{235}U and ^{238}U separated isotopes. The two separated isotopes, in the form of U_3O_8, were dissolved in HNO_3 and filtered to remove small amounts of undissolved material. Impurities were determined by spark source isotope dilution mass spectrometry. No impurities were found at levels that would interfere with either the assay or mass spectrometric measurements. After determining the approximate concentration of the two separated isotopes from preliminary mixes, aliquants for the assay and calibrated mixes were taken by mass. Seven assay aliquants were taken first, then aliquants for the three calibration mixes and finally seven more assay aliquants. The three calibration mixes were prepared to have one mix at approximately the same $^{238}U/^{235}U$ ratio as natural uranium, one to be approximately 0.5 percent more and the third to be approximately 0.5 percent less. Each calibration mix was evaporated to dryness, dissolved and diluted with 0.8M HNO_3 to give a solution containing 1 mg U/g and submitted along with the NDA sample solutions for mass spectrometric analysis. The assay samples were transferred to 180 mL tall form glass beakers and submitted for analysis.

The NBL high precision titration for uranium requires gram amounts of uranium for precisions of ≥ 0.005 percent. Features of this procedure have been adapted to the conditions of the standard NBL titration (approx. 100 mg U) to produce a hybrid version which has precision of better than 0.01 percent compared to the usual 0.05 percent. All techniques and reagents are identical to the published New Brunswick Laboratory methods (9). However, to achieve reductions in the chemical blank and improvements in the sharpness of the potentiometric end point, both the apparatus and reagents have been scaled down.

The best precision was obtained when reagent volumes were scaled to one-half their normal size. At one-fourth scale, problems in adequate rinsing (e.g., 1.3 mL reagent rinse for a 60 mL beaker) are probably responsible for a lack of improvement in precision. Consequently, all controls (SRM 960) and samples were aliquanted to contain approximately 80 mg of uranium in a 180 mL tall form beaker. Titrations indicated essentially a fixed uncertainty over a sample range of 50-125 mg of uranium. Mechanical pipet aids were used to deliver the non-standard reagent volumes (e.g., 2.5 mL) required for the scaled down titration.

The chemistry of the titration is as follows. An excess of ferrous sulfate is employed to reduce U(VI) to U(IV) in a concentrated phosphoric acid solution containing sulfamic acid. The excess ferrous ion is selectively oxidized by nitric acid in the presence of Mo(VI) as a catalyst. Cold water and vanadyl sulfate quench the oxidation and prepare the sample for titration. The U(IV) must be titrated within 2-3 minutes using standard SRM potassium dichromate and a potentiometric end point.

To improve titration precision, two weight burets were used to dispense a concentrated and a dilute dichromate solution into the sample to potentials of 480 and 550 mV, respectively. A dilute dichromate solution was added in increments of 50 uL by a calibrated repeating pipet and potential measurements were made after each addition up to approximately 650 mV. The end point was calculated by means of second derivative determination and the equivalent amount of uranium was computed.

Under these conditions, the assay of SRM 960 averaged approximately 99.99 percent, thus, displaying a relatively constant bias of -0.01 percent throughout all titrations. Since the modified titration required 5-7 minutes to complete, it is believed that air oxidation of U(IV) provided a slight competition for the dichromate ion. Nevertheless, both within and between set precisions were 0.01 percent or less for all of the samples and SRM 960 controls. Samples of the two isotopes and SRM 960 were run in batches in order to average out small day-to-day variations in the apparent recoveries of SRM 960. Because of this, biases in the determined ratio of the concentrations of the two major isotope solutions should be insignificant.

All of the NBS mass spectrometry results are given in Tables 28-32.

5.2.5 Uncertainties in the Isotopic Ratios and Abundances

The 1s uncertainties reported in Tables 28-32 and Table 37 represent the statistical uncertainty of replicate ratio measurements of the material and are thus a precision statement only, since they do not take into consideration uncertainties associated with possible sources of systematic error.

The 2s uncertainties reported in Tables 36 and 39 include terms for known sources of systematic errors and other sources of random errors associated with the measurements, and are thus reflective of the accuracy of the measurements. These uncertainties were calculated from the following formula:

$$2s = (A^2 + B^2 + C^2)^{1/2}$$

where A is the 2s uncertainty on the measured isotopic ratio, B is the 2s uncertainty on the isotopic fractionation correction (K factor) used to place the measurements on an absolute basis, and C is the 2s uncertainty on the standard or synthetic mixes used to obtain the isotopic correction factor. This term also includes components to cover the uncertainties in the isotopic composition and assay of the separated isotopes used in the preparation of synthetic mixes. In all cases, the stated uncertainties reported in Tables 36 and 39 are at least as large as the uncertainties calculated by the NBS Statistical Engineering Division. In some cases, the uncertainties have been expanded at the discretion of the analysts.

Table 28. NBS Measured Isotope Abundances for the 031 Material (atom percent)

Sample #	238	236	235	234
1	99.66228	0.014684	0.321033	0.002006
2	99.66250	0.014810	0.320705	0.001982
3	99.66228	0.014863	0.320881	0.001977
4	99.66270	0.014740	0.320575	0.001984
5	99.66291	0.014555	0.320530	0.002004
6	99.66224	0.014772	0.321005	0.001987
7	99.66250	0.014693	0.320808	0.002002
8	99.66292	0.014558	0.320536	0.001984
9	99.66260	0.014906	0.320501	0.001994
10	99.66275	0.014755	0.320492	0.001999
11	99.66197	0.014817	0.321208	0.002004
12	99.66235	0.014822	0.320832	0.001999
Ave atom%	99.66250	0.014748	0.320759	0.001994
Std. Dev.	0.00014	0.000110	0.000240	0.000010
Ave mass%	99.66669	0.014624	0.316721	0.001960

Atomic Weight = 238.0408

Table 29. NBS Measured Isotope Abundances for the 071 Material (atom percent)

Sample #	238	235	234
22-1	99.27421	0.72050	0.00529
22-2	99.27392	0.72077	0.00531
22-3	99.27384	0.72079	0.00536
22-4	99.27391	0.72080	0.00529
27-col-1[*]	99.27379	0.72086	0.00535
27-col-2	99.27409	0.72056	0.00535
28	99.27392	0.72076	0.00532
32	99.27406	0.72060	0.00534
32-col	99.27411	0.72054	0.00535
Ave atom%	99.27398	0.72069	0.00533
Std. Dev.	0.00014	0.00014	0.00003
Ave mass%	99.28311	0.71165	0.00524

Atomic Weight = 238.0289

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[*] Initial measurements on this material, using the uranyl nitrate dihydrate sample loading procedure, produced abnormal mass specrometric behavior, indicating possible interferences from chemical impurities. To ensure that this problem would not bias the measurements using the UO_3 sample loading procedure, three samples (designated by -col) were further purified with an anion exchange column.

Table 30. NBS Measured Isotope Abundances for the 194 Material
(atom percent)

Sample #	238	236	235	234
41	98.01538	0.00031	1.96651	0.01780
42	98.01538	0.00031	1.96664	0.01766
43	98.01573	0.00029	1.96647	0.01750
44	98.01572	0.00029	1.96641	0.01758
45	98.01529	0.00033	1.96674	0.01764
46	98.01578	0.00031	1.96629	0.01762
47	98.01558	0.00033	1.96644	0.01764
48	98.01620	0.00029	1.96595	0.01755
49	98.01542	0.00030	1.96656	0.01772
50	98.01531	0.00035	1.96648	0.01785
51	98.01579	0.00028	1.96606	0.01787
52	98.01619	0.00031	1.96567	0.01783
Ave atom%	98.01565	0.00031	1.96635	0.01769
Std. Dev.	0.00017	0.00002	0.00031	0.00012
Ave mass%	98.04029	0.00031	1.94200	0.01740

Atomic weight = 237.9909

Table 31. NBS Measured Isotope Abundances for the 295 Material
(atom percent)

Sample	238	236	235	234
61	96.98113	0.00323	2.98670	0.02894
62	96.98067	0.00329	2.98715	0.02888
63	96.98154	0.00343	2.98621	0.02882
64	96.97945	0.00320	2.98817	0.02868
65	96.98058	0.00332	2.98725	0.02886
66	96.98082	0.00332	2.98689	0.02897
67	96.98102	0.00326	2.98705	0.02867
68	96.98127	0.00326	2.98671	0.02876
69	96.98153	0.00323	2.98667	0.02858
70	96.98140	0.00332	2.98638	0.02891
71	96.98151	0.00329	2.98636	0.02885
72	96.98145	0.00326	2.98675	0.02855
Ave atom%	96.98103	0.00328	2.98686	0.02879
Std. Dev.	0.00033	0.00006	0.00052	0.00014
Ave mass%	97.01817	0.00325	2.95026	0.02832

Atomic Weight = 237.9597

Table 32. NBS Measured Isotope Abundances for the 446 Material (atom percent)

Sample #	238	236	235	234
81	95.44199	0.00695	4.51435	0.03670
82	95.44130	0.00700	4.51464	0.03707
83	95.44302	0.00699	4.51289	0.03710
84	95.44400	0.00695	4.51248	0.03655
85	95.44190	0.00700	4.51418	0.03692
86	95.44359	0.00695	4.51257	0.03673
87	95.44235	0.00695	4.51418	0.03652
88	95.44292	0.00695	4.51339	0.03674
89	95.44173	0.00695	4.51434	0.03697
90	95.44222	0.00695	4.51413	0.03670
91	95.44201	0.00691	4.51420	0.03688
92	95.44206	0.00670	4.51442	0.03652
Ave atom%	95.44242	0.00694	4.51381	0.03678
Std. Dev.	0.00076	0.00008	0.00077	0.00020
Ave mass%	95.49756	0.00688	4.45937	0.03618

Atomic Weight = 237.9133

5.3 Measurements Made at NBL by Mass Spectrometry

Four 0.025-g samples of each material were weighed into beakers. The oxide was prepared by NBL's standard mass spectrometry procedure (9). Each sample loading was considered a separate determination, two filaments per analysis using a triple filament ion source. The analysis plan was as follows:

Analysis No.	Material	Determinations
1	NBS SRM 005	1 & 2
2	U 0315	1 & 2
3	U 0315	3 & 4
4	NBS SRM 005	3 & 4
5	U 0715	1 & 2
6	U 0715	3 & 4
7	NBS SRM 010	1 & 2
8	NBS SRM 020	1 & 2
9	U 195	1 & 2
10	U 195	3 & 4
11	NBS SRM 020	3 & 4
12	NBS SRM 030	1 & 2
13	U 295	1 & 2
14	U 295	3 & 4
15	NBS SRM 030	3 & 4
16	NBS SRM 050	1 & 2
17	U 446*	1 & 2
18	U 446*	3 & 4
19	NBS SRM 050	3 & 4
20	U 446*	5 & 6
21	U 446*	7 & 8
22	NBS SRM 050	5 & 6

The asterisk (*) indicates that series 445 samples were not available at the same time that the other samples were analyzed. However, they were analyzed later in a similar manner and bracketed with NBS SRM 050.

The results of these analyses are given in the following Table 33.

5.4 CBNM Gamma Spectrometry Measurements

A high resolution gamma spectrometry system with a full width at half maximum (FWHM) of 0.83 keV at 185.7 keV, Figure 2., was used to determine the overall uniformity of the entire 140 sets of reference materials.

5.4.1 Measurement of all of the Canned Reference Materials

All 140 of the fabrication samples from each of the five materials were tested by gamma counting the ^{235}U 185.7 keV gamma-ray, using a Pb collimator 25 mm in diameter and 40 mm in height. These gamma measurements were all low precision with 1 relative standard deviation (RSD) between ±0.5% and ±0.9%, and were made relative to a calibration sample with a ^{235}U isotope abundance of

Table 33. Uranium Isotopic Abundances Determined by NBL

Sample (n)		234	235	236	238	Rel. At. Wt.
031 (4)	mass%	0.0022	0.3163	0.0145	99.6670	238.0408
	sd	0.0002	0.0002	0.0002	0.0002	
	atom%	0.0022	0.3203	0.0147	99.6628	
071 (4)	mass%	0.0053	0.7116	0.0000	99.2831	238.0289
	sd	0.0002	0.0002		0.0003	
	atom%	0.0054	0.7207	0.0000	99.2739	
194 (4)	mass%	0.0175	1.9414	0.0003	98.0407	237.9910
	sd	0.0004	0.0005	0.0003	0.0009	
	atom%	0.0178	1.9657	0.0003	98.0161	
295 (4)	mass%	0.0280	2.9477	0.0030	97.0213	237.9599
	sd	0.0002	0.0012	0.0004	0.0015	
	atom%	0.0284	2.9843	0.0030	96.9843	
446 (8)	mass%	0.0361	4.4617	0.0063	95.4958	237.9134
	sd	0.0003	0.0015	0.0004	0.0014	
	atom%	0.0367	4.5162	0.0064	95.4407	
SRM U-005	mass%	0.0024	0.4835	0.0045	99.5096	238.0359
(5)	sd	0.0002	0.0002	0.0003	0.0003	
	atom%	0.0024	0.4897	0.0046	99.5033	
SRM U-010	mass%	0.0056	0.9911	0.0067	98.9967	238.0203
(2)	sd	0.0001	0.0002	0.0003	0.0003	
	atom%	0.0057	1.0036	0.0067	98.9840	
SRM U-020	mass%	0.0123	2.0122	0.0166	97.9590	237.9887
(4)	sd	0.0002	0.0005	0.0002	0.0004	
	atom%	0.0125	2.0374	0.0167	97.9334	
SRM U-030	mass%	0.0189	3.0085	0.0203	96.9524	237.9580
(4)	sd	0.0003	0.0007	0.0003	0.0007	
	atom%	0.0192	3.0458	0.0205	96.9146	
SRM U-050	mass%	0.0275	4.9497	0.0475	94.9753	237.8981
(6)	sd	0.0005	0.0016	0.0005	0.0020	
	atom%	0.0280	5.0098	0.0479	94.9194	

2.98 atom %, to minimize the effect of detector efficiency shifts. Figures 15a - 19a illustrate the statistical distribution of the counting rates of all the cans within a given abundance. In addition, the agreement shown between the distribution of the mean counting rate value and the counting precision of single measurements, represented by the shaded area, confirmed the statistical nature of the measured distribution, as well as monitored the uniformity of the samples during the canning process.

Two types of samples were selected from the low precision measurements for confirmation of sample uniformity and for high precision measurements:

- samples with counting rates approximately equal to the mean counting rate;
- samples with counting rates at the high and low ends of the distribution.

Some of these low precision samples comprised the 24 samples per material that were sent to NBS and to another Joint Research Center within the European Community, JRC-Ispra Establishment, for gamma spectrometry measurements.

5.4.2 High Precision Measurements of the 15 Selected Samples

The 15 samples from each of the five materials were selected from the center and tails of the counting rate distributions presented in Figures 15a - 19a. These cans were measured under the same conditions as before but with precisions (RSD) between ±0.16% and ±0.29%. The results of the high precision measurements, as seen in Figures 15b - 19b, confirm the can to can sample uniformity observed in the low precision measurements.

5.4.3 High Precision Measurements of the 446 Material

The counting rates of all 140 samples from the 446 material were measured relative to one of the samples in the series. These samples were remeasured under conditions described earlier except for a Pb collimator 30 mm in diameter and 40 mm in height, and a 1 RSD measurement precision of ±0.14%. The measurement distribution curve in Figure 20 compares the statistical distribution to the counting precision of a single measurement. The shaded area also confirms the sample to sample uniformity that had been discussed above, in sections 1 and 2.

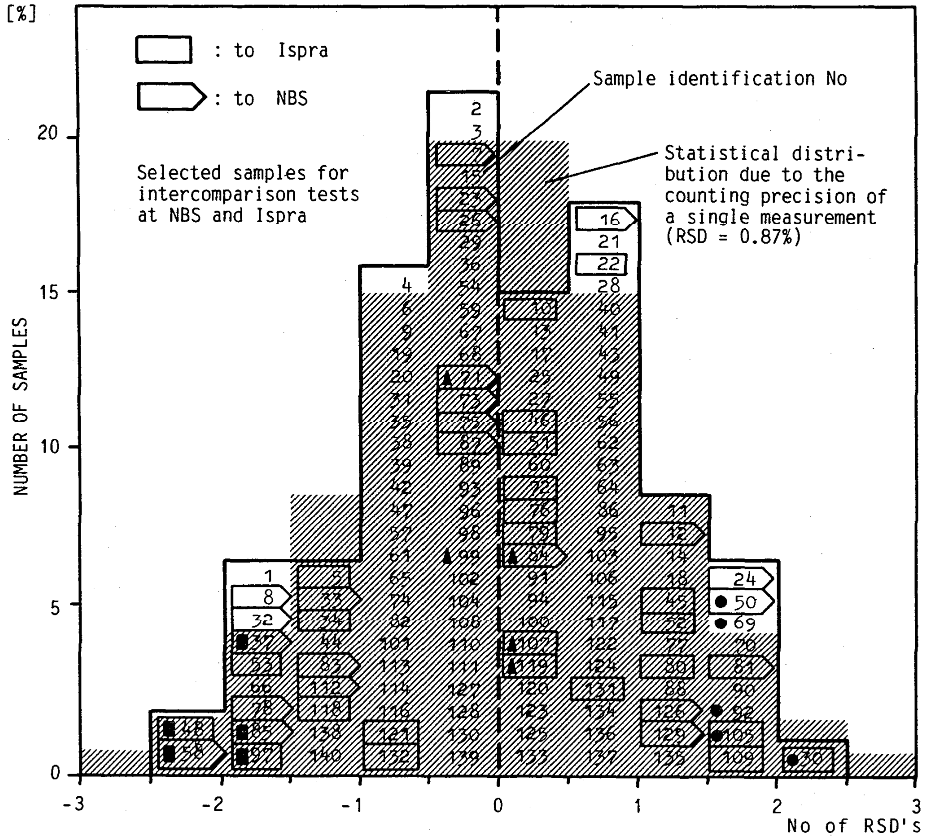
The results of these measurements indicate the sample to sample non-uniformity was less than the calculated value of ±0.14% which was projected in section IV.K.3.

5.4.4 Determining the Linearity of the Sets

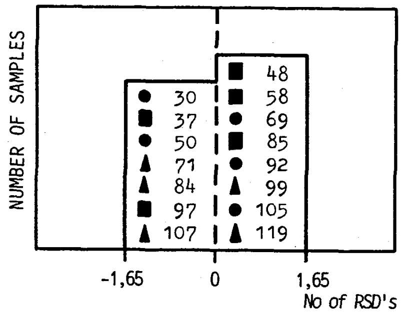
High precision gamma measurements, using the same conditions as in 3, were made on the 50 CBNM sets fitted with ultrasonic seals. These measurements were made with a 1 RSD counting precision proportional to the ^{235}U isotope abundance in atom percent, (A_v) of each material, such that 1 RSD % $\leq \pm\ 0.5 \times (0.25 + 0.1/A_v)$.

The observed counting rate for each material (n) was normalized to its $^{235}U/U$ abundance $[(A_v)_n]$ and corrected for the interference (Ky) from the ^{234}Pa and ^{234m}Pa daugthers of ^{238}U

$$C_n = \frac{C_n^o \cdot Ky_n}{(A_v)_n} \tag{9}$$



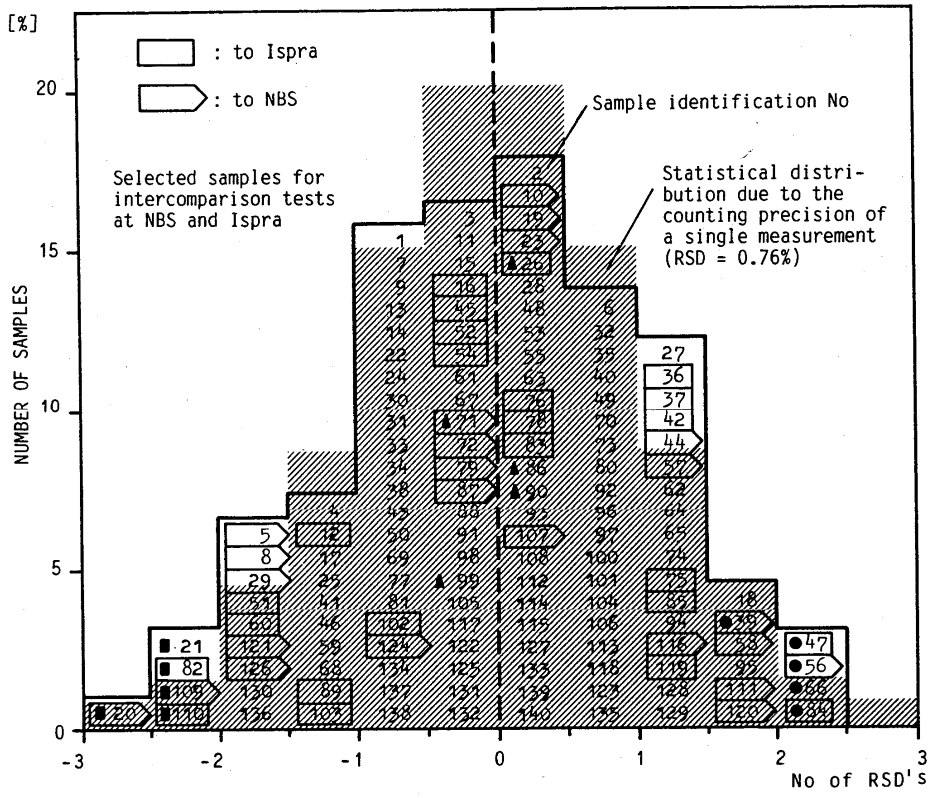
a. Low precision test of samples (RSD = 0.87%)



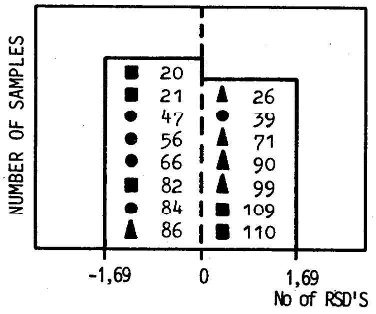
b. High precision test of samples (RSD = 0.28%) as identified above

Figure 15. Gamma Counting Rate Uniformity of U_3O_8 Reference Samples at 1857 keV (corrected for window thickness)

- $^{235}U/U = 0.003207$
- Germanium detector Ø: 50 mm; h: 15 mm with resolution (FWHM) of 0.83 keV
- Collimator Ø: 25 mm; h: 40 mm



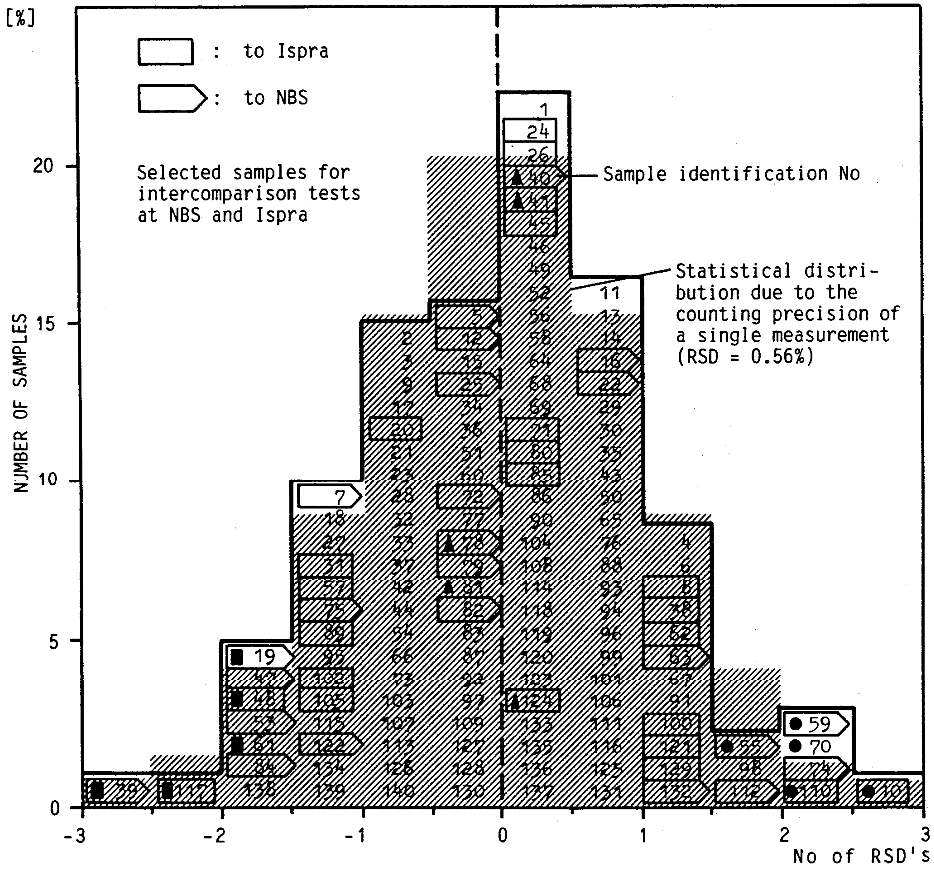
a. Low precision test of samples (RSD = 0.76%)



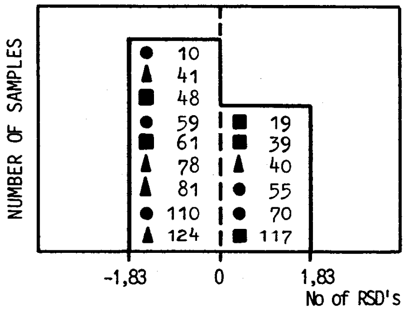
b. High precision test of samples (RSD = 0.29%) as identified above

Figure 16. Gamma Counting Rate Uniformity of U_3O_8 Reference Samples at 185.7 keV (corrected for window thickness)

- $^{235}U/U = 0.07208$
- Germanium detector Ø: 50 mm; h: 16 mm with resolution (FWHM) of 0.83 keV
- Colliminator Ø: 25 mm; h: 40 mm



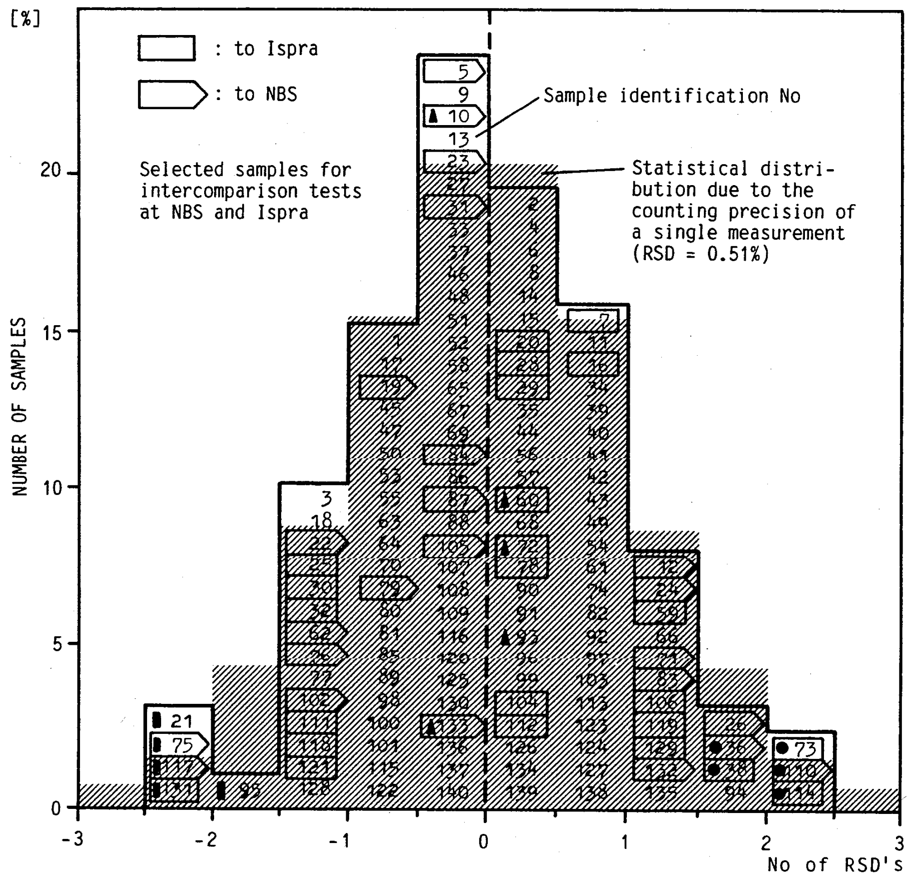
a. Low precision test of samples (RSD = 0.56%)



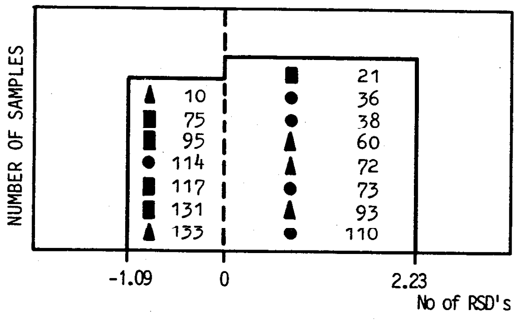
b. High precision test of samples (RSD = 0.19%) as identified above

Figure 17. Gamma Counting Rate Uniformity of U_3O_8 Reference Samples at 185.7 keV (corrected for window thickness)

- ^{235}U/U = 0.01967
- Germanium detector Ø: 50 mm; h: 16 mm with resolution (FWHM) of 0.83 keV
- Colliminator Ø: 25 mm; h: 40 mm



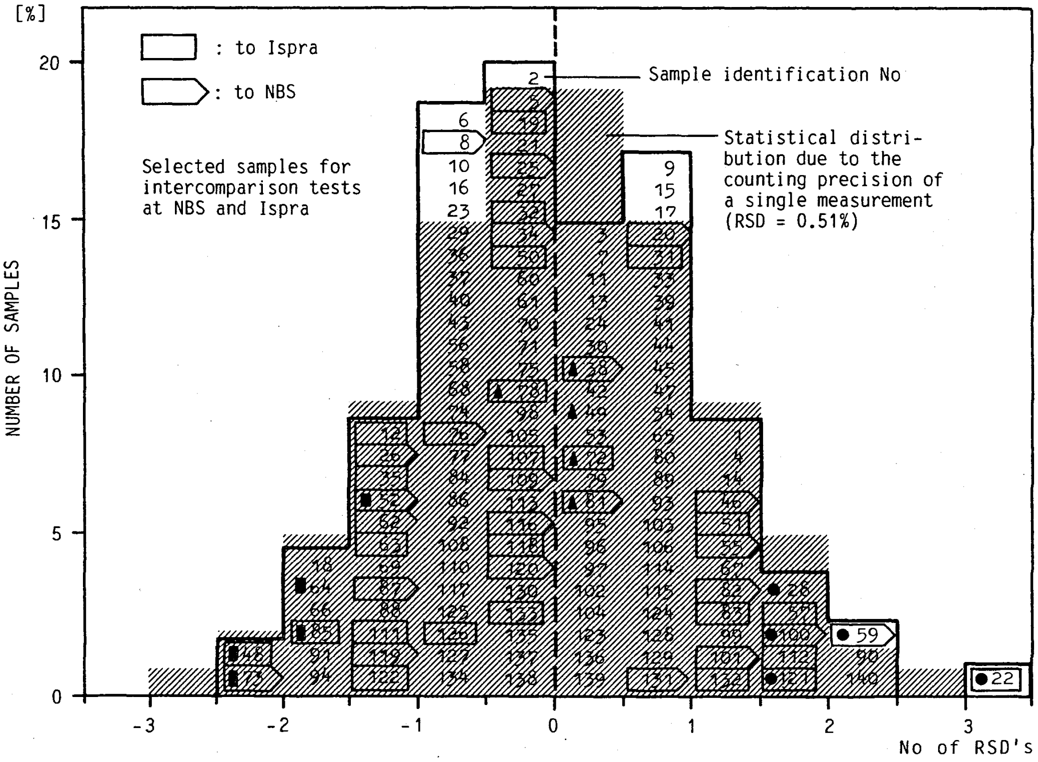
a. Low precision test of samples (RSD = 0.51%)



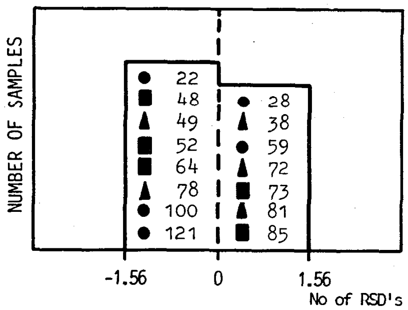
b. High precision test of samples (RSD = 0.21%) as identified above

Figure 18. Gamma Counting Rate Uniformity of U_3O_8 Reference Samples at 185.7 keV (corrected for window thickness)

- $^{235}U/U = 0.02985$
- Germanium detector Ø: 50 mm; h: 16 mm with resolution (FWHM) of 0.83 keV
- Colliminator Ø: 25 mm; h: 40 mm



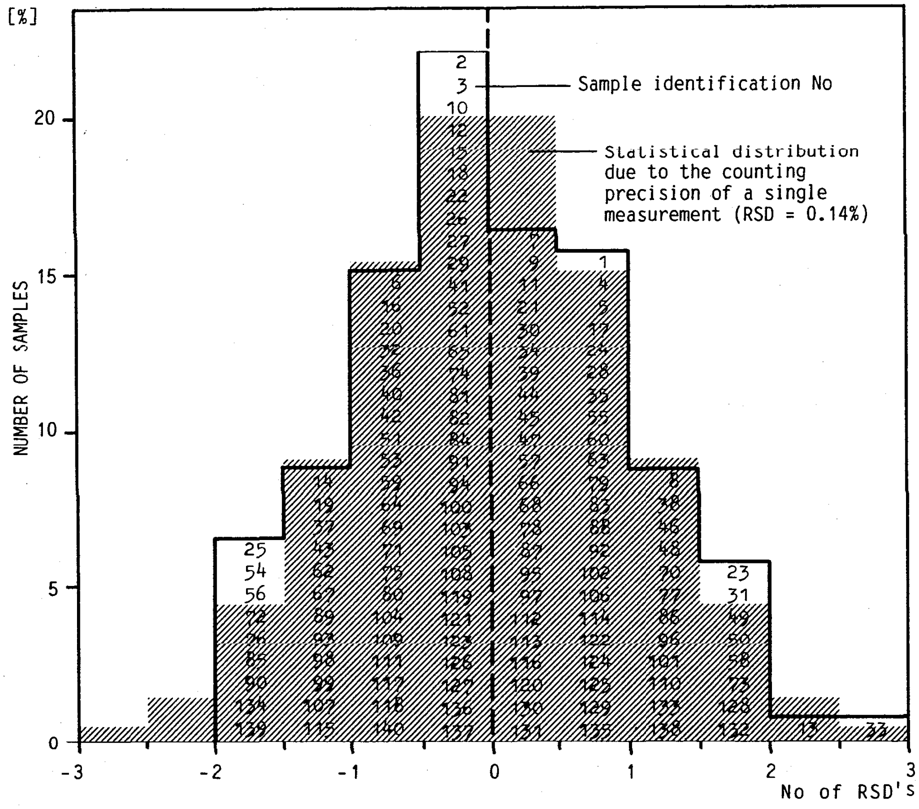
a. Low precision test of samples (RSD = 0.51%)



b. High precision test of samples (RSD = 0.16%) as identified above

Figure 19. Gamma Counting Rate Uniformity of U_3O_8 Reference Samples at 185.7 keV (corrected for window thickness)

- ^{235}U/U = 0.04518
- Germanium detector ∅: 50 mm; h: 16 mm with resolution (FWHM) of 0.83 keV
- Colliminator ∅: 25 mm; h: 40 mm



No° or samples : 140
Detector : Germanium, ∅:50 mm; h:16mm
Detector resolution (FWHM) : 0.83 keV for 185.7 keV....
Collimator : ∅:30 mm; h:40 mm

Figure 20. High Precision Test of the Gamma Counting Rate Uniformity of U_3O_8 Reference Samples, $^{235}U/U = 0.04518$, at 185.7 keV

where C_n is the corrected counting rate for each of the five materials and C_n^o is the weighted average of the observed counting rates (uncorrected) for the individual samples of material n.

The deviation (dC_n) for each material compared to the average value for all five materials (C) was calculated and normalized to C and these values are plotted in Figure 21.

$$\frac{dC_n}{C} (\%) = 100 \cdot \left(\frac{C_n - C}{C} \right) \qquad (10)$$

This figure illustrates the linearity of the calibration curve for the particular instrumentation system used as well as the agreement between ratios of the ^{235}U isotope abundance values obtained from the mass spectrometry measurements and the corresponding ratios of the measured gamma counting rates.

5.5 NBS Gamma Spectrometry Measurements

All of the NBS verification and isotope abundance measurements by gamma spectrometry were made on a counting system that consisted of an Ortec Gamma X type high purity germanium detector, a Canberra 3105 high voltage supply, a Canberra 2021 S amplifier and a Nuclear Data ND 6620 computer-based analyzer system. The amplifier time constant was set at 6 us, and an ADC conversion gain of 8192 channels was used. At low counting rates, this system has a resolution of 1.69 keV full width at half maximum (FWHM) for the 1332 keV gamma ray of ^{60}Co and an efficiency of 7.99% relative to a 3"x3" NaI(Tl) detector at 25cm. The resolution observed in this work for the 185.7 keV gamma ray of ^{235}U varied from 0.95 keV (FWHM) for the 031 sample samples(15% dead time) to 1.00 keV for the 446 sample series (22% dead time). Separation of the 182.57 and 185.7 keV gamma rays was such that the channel between these peaks contained approximately 0.02% (above background) of the net 186 keV peak region counts. The 071, 194, 295 and 446 sample series were counted for times sufficient to accumulate approximately 5 x 10^6 net counts in the 186 keV peak region (2-12 hours live time). The counting statistics observed for the 186 keV peak region were typically 0.04-0.06%. The 031 samples were counted overnight which produced approximately 2.5 x 10^6 net counts in the 186 keV peak region. Typically the observed counting statistics for the 031 samples were 0.10%.

In order to ensure reproducibility in geometric positioning of the cans for counting, a collimator assembly was fabricated from lead for this work (see Figure 2a). A U-shape configuration with a diameter of 81 mm and a depth of 35mm was machined into the top surface of the lead to allow a rigid resting place for the aluminum cans, and to maintain an identical counting geometry from one sample to another. The collimator opening was then machined to a 50mm diameter with a 15mm thickness. A copper plate (12cm x 12cm x 6 mm) with a 70 mm diameter opening, for the high purity germanium detector endcap, was then affixed to the base of the collimator. This entire assembly was then fitted with four mounting screws, allowing the assembly to be supported by the floor of the detector shield and not by the detector.

The counting standards used in this work consisted of a set of three prototype 200g U_3O_8 samples which had previously been developed to determine the feasibility of the program. These counting standards were prepared by CBNM

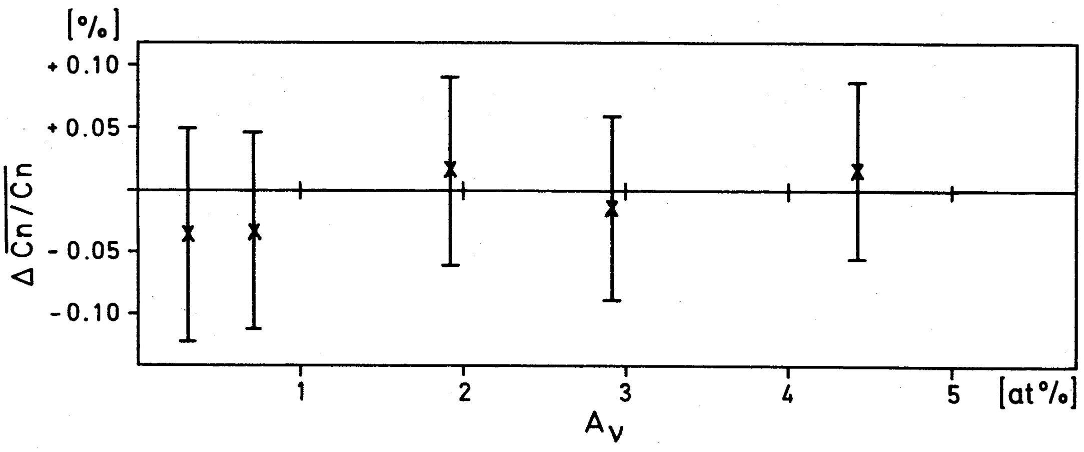


Figure 21. Average Variation of Normalized Gamma Counting 4ates at 185.7 keV versus ^{235}U Abundance, A_V, for the CBNM 50 Sets of Samples (Uncertainies are 2s and Include the Mass Spectrometry Uncertainties of A_V of 0.07%

(4) in the same manner as the reference materials with the exception of the aluminum containers. The prototype cans were fabricated with flat bottoms, while the reference material cans were produced with 1mm recessed bottoms to minimize scratching of the can windows. The isotope measurements of these samples were performed and certified by CBNM to have $^{235}U/U$ atom percent abundances of 2.9788 ± 0.0090, 0.7201 ± 0.0021 and 0.02978 ± 0.0009, respectively, and were identified as SD-524, SD-528, and SD-521. In addition, verifying gamma spectrometry measurements were also performed on the samples by NBS and CBNM. Although all three counting standards were used during the course of this work, the primary counting standard was considered to be the 2.9788 atom percent sample (SD-524).

5.5.1 Peak Integration Methods

Three different methods were used to integrate the 185.7 keV ^{235}U peak: a Gaussian fitting routine; a channel by channel doublet summation of the combined 183 (small) and 186 keV peak regions, and a channel by channel singlet summation of the 186 keV peak region alone. The channel between the 183 and 186 keV peak regions (containing 0.02-0.03% of the net counts in the 186 keV peak region) was included as part of the 186 peak region for the singlet summation. Both peak and background regions for the two summation methods were selected symmetrically around the 185.7 keV peak centroid. See Figure 22.

Of the three methods used for peak integration (see Table 34 for examples of the results for a single series using all three methods), it was expected that the summation methods would be better than the Gaussian fitting for a number of reasons. Gaussian fitting introduces added uncertainties since gamma-ray peaks are not fully Gaussian. In addition, the integration routine can choose different peak boundaries for the samples and standards further increasing the uncertainty. The singlet method is somewhat sensitive to changes in the width of the 186 kev peak region between sample and standards. The results obtained for the five series using the three methods are listed in Table 35. However, since the set of five samples were all compared to the same standard and some differences were observed in peak width, the doublet summation method is considered to be the most accurate. However, within a single set of samples the singlet method provides the best measure of precision since the doublet method includes a number of background channels as part of the peak which contributes to poorer counting statistics.

5.5.2 Corrections Applied to Gamma Measurements

Several corrections were applied to the observed counting rate of the 186 keV peak region. These included corrections for pulse pileup, ^{234}Pa and ^{234m}Pa interference, differences in window thickness of the sample containers, and differences in container geometry for the samples compared to the standards.

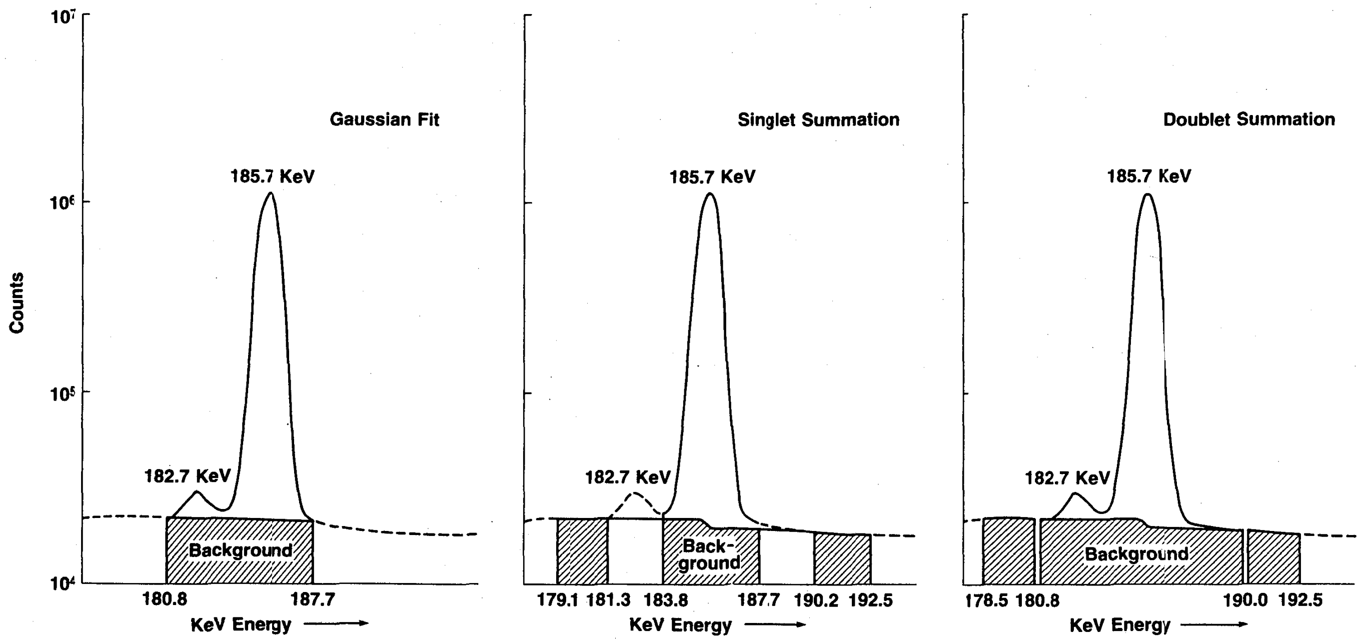


Figure 22. The Three Peak Integration Methods Used a) Gaussian Fit, b) Singlet Summation and c) Doublet Summation

Table 34. ^{235}U Abundances Measured at 185.72 kev Using the Three Integration Methods (atom percent with 1 sigma)

Can Number	Doublet[a]	Singlet[b]	Gaussian[c]
NBS-295-117	2.97941	2.97909	2.97970
CBN-295-005	2.98201	2.98266	2.98248
CBN-295-024	2.98297	2.98305	2.98137
NBS-295-079	2.98465	2.98475	2.98483
NBS-295-075	2.98085	2.98154	2.98200
CBN-295-022	2.98151	2.98102	2.98119
CBN-295-023	2.98195	2.98151	2.98006
NBS-295-071	2.97809	2.97839	2.97908
CBN-295-031	2.98327	2.98289	2.98010
CBN-295-026	2.98498	2.98398	2.98653
CBN-295-036	2.98325	2.98261	2.99087
NBS-295-102	2.98652	2.98524	2.98379
NBS-295-105	2.98059	2.98153	2.98179
NBS-295-110	2.98490	2.98434	2.99165
NBS-295-084	2.98352	2.98281	2.98724
CBN-295-010	2.98300	2.98179	2.98984
NBS-295-083	2.98374	2.98515	2.99325
CBN-295-012	2.98591	2.98585	2.99317
NBS-295-133	2.98179	2.98211	2.98654
NBS-295-076	2.98229	2.98227	2.98691
NBS-295-132	2.98452	2.98455	2.98344
CBN-295-019	2.98364	2.98166	2.99037
NBS-295-087	2.98481	2.98491	2.99344
CBN-295-062	2.98345	2.98291	2.98220
Mean	2.98298	2.98277	2.98549
Sample STD DEV	0.00199	0.00187	0.00476

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[a] Individual Uncertainties ±0.00155
[b] Individual Uncertainties ±0.00144
[c] Individual Uncertainties ±0.00115

Table 35. Summary of ^{235}U Abundances (atom parts per million) for the Three Peak Integration Methods

	Singlet Method			Doublet Method*			Gaussian Method		
Sample	Ave	s	$\bar{s}$%	Ave	s	$\bar{s}$%	Ave	s	$\bar{s}$%
031	3206.9	3.5	0.021	3205.3	4.2	0.025	3206.8	4.9	0.029
071	7212.3	5.2	0.014	7208.1	7.8	0.022	7225.5	9.0	0.025
194	19665.5	10.5	0.011	19660.2	10.9	0.012	19687.5	13.5	0.014
295	29827.7	18.5	0.013	29829.7	20.0	0.014	29854.8	47.6	0.033
446	45142.5	26.5	0.012	45157.8	27.9	0.013	45139.9	63.3	0.030
521	2974.9	1.7	0.029	2972.8	2.3	0.039	2974.6	2.6	0.044
528	7217.4	2.1	0.015	7214.3	2.8	0.019	7230.0	3.2	0.022

* Recommended values.
- A 0.1 ppm ^{235}U background has been subtracted from these results.

The pulse pileup correction was made according to equation 11.

$$I_o = I \exp [C(R-L)/L] \qquad (11)$$

where I_o = corrected intensity
I = observed intensity
C = pileup constant
R = real (clock) time
L = live time

In view of the unusual spectral shape of the collimated uranium samples, the possible variation from the "99.9% infinite thickness," the high detector efficiency for low energy gamma and X-radiation, and the relatively high dead time (15-22%), particular attention was paid to determining the pileup constant. To determine this constant, the three prototype standards were counted on a second analyzer system for which the pileup correction was much less important, and the activity ratios were compared to those observed with the main system. This second system contained a collimator with a much smaller opening to reduce the counting rate, a Ge(Li) detector with normal (low) efficiency for low energy radiation, and an amplifier whose time constant was set at 2 us. With this system, the pileup correction ranged from 1.012 for the SD-521 (0.2978 atom % ^{235}U) sample to 1.014 for the SD-524 (2.9788 atom % ^{235}U) sample; dead times were between 4.2 and 5.1%. Since the pileup corrections were similar, small errors in the pileup constant of this (second) system were negligible; a 1% error in the pileup constant would only produce a 0.002% error in the activity ratios. The pileup constant for the main system was then calculated by comparing the activity ratios observed for the two systems.

Both the ^{234}Pa and ^{234m}Pa daughters of ^{234}Th in the ^{238}U decay chain have gamma rays very close to the 185.7 keV gamma ray of ^{235}U, and thus interfere with the ^{235}U determination (see Figure 24). The magnitude of this interference was determined by using a specially prepared sample containing 200 grams of NBS SRM U-0002 which is certified to have a ^{235}U isotope abundance of 0.01755 ± 0.00005 atom percent. This sample was counted using the same facilities as the SRM 969/EC 171 samples. After correcting for the ^{235}U isotope abundance in this highly depleted sample, the 186/258 peak region ratio was used to remove the Pa interference from the uranium reference materials. Since the correction was made totally from Pa gamma rays, establishment of equilibrium between ^{238}U and ^{234}Th was not necessary.

The 186/258 peak region ratios were determined (and applied) separately for each of the summation methods. Since both summation methods used the same peak and background channels for the depleted U_3O_8 and the samples, the correction based on the 186/258 peak region ratio should also minimize possible spectrum shape effects due to the background from the ^{238}U content of the samples.

Although differences in window thickness among samples (and standards) were small ($\leq$ 0.1 mm), corrections for the attenuation of the 185.7 keV gamma ray by the aluminum cans were necessary and were applied according to equation 12.

$$R_c = R_o\ (1 + 0.034\ dt) \qquad (12)$$

where R_c = Sample counting rate corrected for thickness difference
R_o = Observed sample counting rate
dt = Thickness difference between sample and standard

where 0.034 is the total linear attenuation coefficient at 185.7 keV for aluminum.

A correction was necessary for the geometry difference between the cans of the samples and the standards. The sample cans have a 1.0 mm lip (to protect the thin window) while the SD standards have a flat bottom. A 1.0mm spacer was prepared approximating the difference between the types of cans, and the SD 524 standard was counted with and without the spacer, three times each, alternating between geometries. Approximately 5 x 10^7 counts were obtained in the 186 keV peak region for each counting period and the ratio of the counts in the two positions was used to obtain the 0.214% correction for the geometry difference.

It was necessary to make a correction for the higher packing density of the 446 samples compared to the packing densities of the 031 - 295 samples as well as the prototypes samples. As discussed above when the sample container was raised 1 mm the counting rate decreased by 0.214 %. However, the higher packing density of the 446 samples caused a higher counting rate than the other samples, since on the average these samples were closer to the detector than the others. A direct calculation of this correction factor was difficult, therefore, it was approximated by comparing the "average heights" (the level of 50% attenuation of the 185.7 keV gamma ray) between samples and standards. The thickness of U_3O_8 necessary for 50% attenuation was calculated from equation 13.

$$I/I_o = 0.50 = \exp(-\ 1.263\ t_{50}) \tag{13}$$

where I = observed intensity of the 185.7 keV gamma ray
I_o = intensity of the 185.7 keV gamma ray with no absorption
t_{50} = thickness of U_3O_8 needed to absorb 50% of the emitted gamma rays and with 1.263 being the attenuation coefficient of U_3O_8 in cm^2/g.

This 50% thickness (in g/cm^2) was converted to the "average height" by dividing by the packing densities of the 446 samples and the standard. The difference in this average height was 0.5811 mm. This value was multiplied by 0.214% per 1 mm to arrive at the -0.1244% correction used for the higher packing density of the 446 samples. It should be noted that this correction is collimator specific.

6. Conclusion and Discussion of Results

The ratios of $^{235}U/^{238}U$ determined by each mass spectrometry laboratory are given in Table 36. These measurements reflect both laboratory methods, thermal ionization mass spectrometry and UF_6 mass spectrometry. Individual laboratory determinations of the abundances of other U isotopes are listed in Table 37, and the mean values are listed in Table 38. It should be noted that the summary of values given in Table 37 are only from thermal ionization mass spectrometry measurements since UF_6 mass spectrometry only provided $^{235}U/^{238}U$ ratio measurements. Therefore, the values for the ^{234}U and ^{236}U isotope abundances were determined from the CBNM and NBS ThIMS measurements. These abundances are presented on the certificate as well as in Table 38.

Table 36. $^{235}U/^{238}U$ Mass Spectrometry Ratios with 2s Uncertainties (x100)

Laboratory-Method	Material				
	031	071	194	295	446
CBNM-UF_6	0.32157 ±0.00016	0.72623 ±0.00017	2.00552 ±0.00038	3.07711 ±0.00051	4.73248 ±0.00082
CBNM-ThIMS	0.32170 ±0.00048	0.72652 ±0.00100	2.0074 ±0.0018	3.0805 ±0.0042	4.7362 ±0.0057
NBS-ThIMS	0.32184 ±0.00052	0.72596 ±0.00068	2.0062 ±0.0017	3.0798 ±0.0022	4.7294 ±0.0033
NBL-ThIMS	0.32141 ±0.00068	0.72595 ±0.00072	2.0055 ±0.0016	3.0771 ±0.0042	4.7319 ±0.0043

A summary of the $^{235}U/U$ isotope abundance measurements are given in Table 39 by method and laboratory. The measurements made by NBL and NBS gamma are given as independent verification information and are not part of the certified values. The certified values for the ^{235}U isotope abundances of this reference material are based on the CBNM UF_6 and thermal ionization mass spectrometry measurements, and the NBS thermal ionization mass spectrometry measurements. These values were obtained by assigning a one-to-one weight balance to the UF_6MS measurements and to the ThIMS measurements, and also to the average of the CBNM ThIMS measurements and to the NBS ThIMS measurements. The certified values in Table 40 were calculated using Equation 14.

$$^{235}U/U \text{ abundance} = (0.5\cdot A)+(0.25\cdot B)+(0.25\cdot C) \tag{14}$$

where A = represents the CBNM UF_6 measurement values and 2s uncertainties for each $^{235}U/U$ isotope abundance,

B = represents the CBNM ThIMS measurement values and 2s uncertainties for each $^{235}U/U$ isotope abundance,

C = represents the NBS ThIMS measurement values and 2s uncertainties for each $^{235}U/U$ isotope abundance.

Table 37. Summary of Uranium Isotopic Abundance Measurements by ThIMS for ^{234}U, ^{236}U, and ^{238}U

Material	234	236	238	At. Wt.
031				
CBNM-ThIMS				
atom%	0.00201	0.01460	99.66273	238.04087
2s	0.00012	0.00090	0.00091	
NBL				
atom%	0.0022	0.0147	99.6628	238.0408
2s	0.0002	0.0002	0.0002	
NBS				
atom%	0.00199	0.01475	99.6625	238.0408
1s	0.00001	0.00011	0.0001	
071				
CBMN-ThIMS				
atom%	0.00524	<0.00002	99.27389	238.02919
2s	0.00030		0.00035	
NBL				
atom%	0.0054	<0.00002	99.2739	238.0289
2s	0.0002		0.0003	
NBS				
atom%	0.00533	<0.00002	99.27398	238.0289
1s	0.00003		0.00014	
194				
CBNM-ThIMS				
atom%	0.01724	0.00028	98.01505	237.9917
2s	0.00102	0.00005	0.00107	
NBL				
atom%	0.0178	0.0003	98.0161	237.9910
2s	0.0004	0.0003	0.0009	
NBS				
atom%	0.01769	0.00031	98.01565	237.9910
1s	0.00012	0.00002	0.00017	
295				
CBNM-ThIMS				
atom%	0.02799	0.00326	96.98096	237.9609
2s	0.00159	0.00023	0.00165	
NBL				
atom%	0.0284	0.0030	96.9843	237.9599
2s	0.0002	0.0004	0.0015	
NBS				
atom%	0.02879	0.00328	96.98103	237.9597
1s	0.00014	0.00006	0.00033	
446				
CBNM-ThIMS				
atom%	0.03636	0.00687	95.43622	237.9150
2s	0.00208	0.00042	0.00213	
NBL				
atom%	0.0367	0.0064	95.4407	237.9134
2s	0.0003	0.0004	0.0014	
NBS				
atom%	0.03678	0.00694	95.44242	237.9133
1s	0.00020	0.00008	0.00076	

Table 38. Values of Uranium Isotopes, ^{234}U, ^{236}U and ^{238}U, in percent, given on the certificate.

Material		Uranium Isotopes		
		^{234}U	^{236}U	^{238}U
031	atom	0.0020	0.0147	99.6627
	2s	±0.0002[a]	±0.0003	±0.0004
	mass	0.0020	0.0146	99.6668
071	atom	0.0053	<0.00002	99.2738
	2s	±0.0002		±0.0004
	mass	0.0052	<0.00002	99.2828
194	atom	0.0174	0.0003	98.0159
	2s	±0.0002	±0.0001	±0.0018
	mass	0.0171	0.0003	98.0406
295	atom	0.0284	0.0033	96.9826
	2s	±0.0004	±0.0002	±0.0029
	mass	0.0279	0.0033	97.0196
446	atom	0.0365	0.0069	95.4398
	2s	±0.0003	±0.0002	±0.0032
	mass	0.0359	0.0068	95.4950

Table 39. Summary of ^{235}U/U Isotope Abundance Measurements, in Atom Percent with 2s Uncertainties, by Method and Laboratory

Laboratory/Method	Material				
	031	071	194	295	446
CBNM-UF$_6$	0.32049 ±0.00016	0.72096 ±0.00017	1.96575 ±0.00037	2.98432 ±0.00048	4.51668 ±0.00075
CBNM-ThIMS	0.32061 ±0.00047	0.72119 ±0.00098	1.96750 ±0.00173	2.98746 ±0.00390	4.52007 ±0.00519
NBS-ThIMS	0.32076 ±0.00052	0.72069 ±0.00068	1.9664 ±0.0017	2.9869 ±0.0022	4.5138 ±0.0033
NBL-ThIMS	0.3203 ±0.0007	0.7207 ±0.0007	1.9657 ±0.0015	2.9843 ±0.0039	4.5162 ±0.0039
NBS-Gamma	0.32053 ±0.00026	0.72081 ±0.00058	1.9660 ±0.0016	2.9830 ±0.0024	4.5158 ±0.0036

Table 40. Summary of the Certified ^{235}U Isotope Abundance Values, (in percent) and uncertainties (±0.07% on all values)

	Material 031	071	194	295	446
Atom	0.3206	0.7209	1.9664	2.9857	4.5168
±0.07%	±0.0002	±0.0005	±0.0014	±0.0021	±0.0032
Mass	0.3166	0.7119	1.9420	2.9492	4.4623

The overall uncertainty for each of the $^{235}U/U$ certified values was estimated by combining the uncertainties of the mass spectrometry measurements with any possible deviation of the $^{235}U/U$ ratio due to inhomogeneity. The resulting uncertainty for each abundance was enlarged to 0.07%, which corresponds to the 95% confidence limit.

The NBS gamma spectrometry measurements which were not a component of the certified value were found to be within 0.09% of the certified value for the 295 material and 0.02% for the 031, 071, 194 and 446 materials as can be seen in Figure 23. These measurements demonstrate the accuracy that is achievable for $^{235}U/U$ isotope abundance determination by gamma spectrometry.

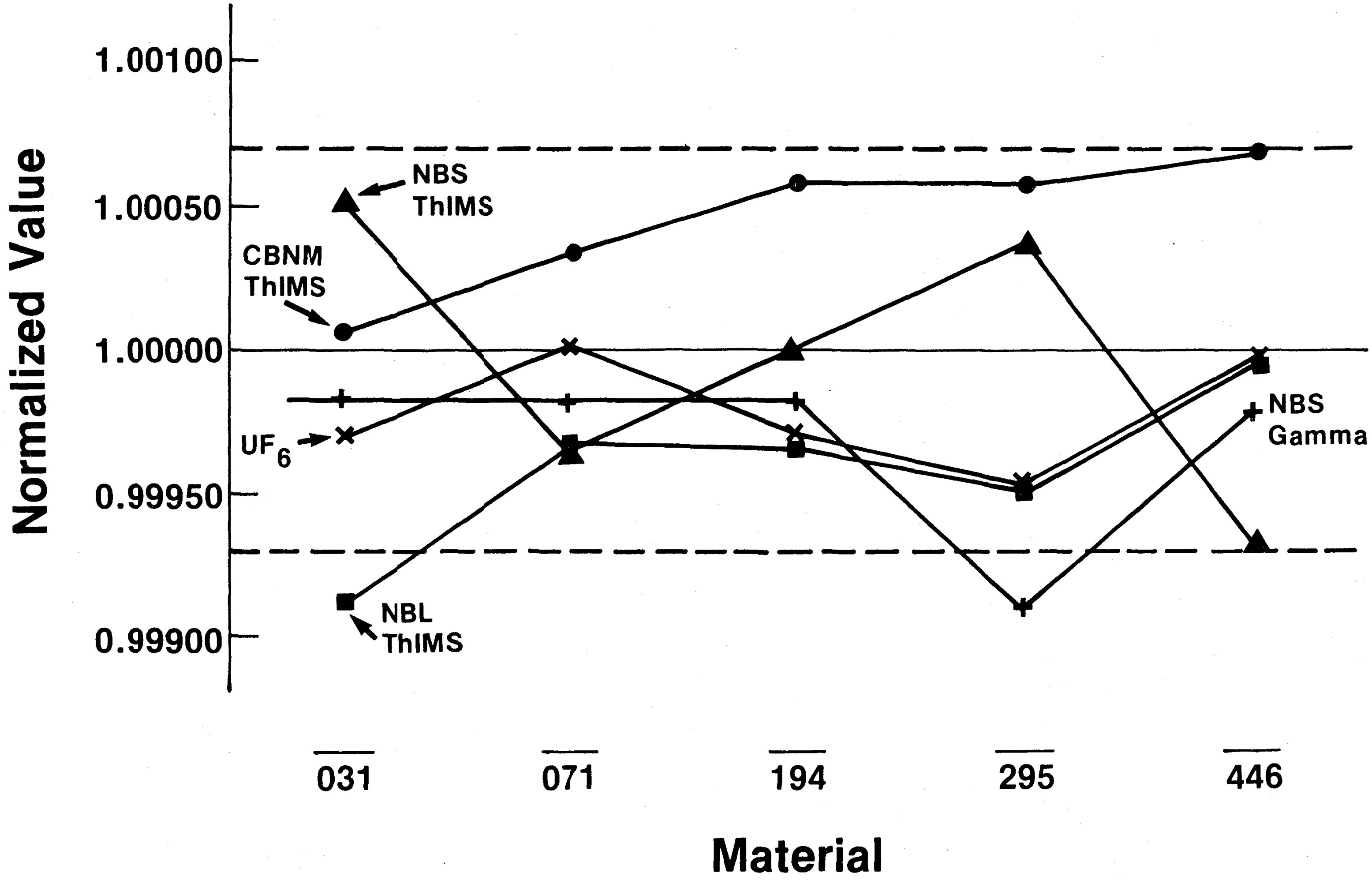

Figure 23. $^{235}U/U$ Measurement by Various Methods Normalized to the Certified Value (- - - - indicates the ±0.07% uncertainty)

7. Acknowledgments

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8. References

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U. S. Department of Commerce
Malcolm Baldrige
Secretary
National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate

Standard Reference Material 969

Uranium Isotopic Standard Reference Material for Gamma Spectrometry Measurements

(In Cooperation with the Commission of the European
Communities, Central Bureau for Nuclear Measurements, Geel,
Belgium, and the U.S. Department of Energy, New Brunswick
Laboratory, Argonne, Illinois.)

This Standard Reference Material (SRM) is intended for use in the calibration and evaluation of gamma-ray counting procedures for the nondestructive determination of the $^{235}U/U$ isotope abundance in uranium bulk materials. SRM 969 consists of a set of five different U_3O_8 powders, with nominal ^{235}U abundances of 0.31, 0.71, 1.94, 2.95, and 4.46 mass percent, encased in aluminum cans that have been manufactured to rigid specifications (See attachments) and thoroughly tested. In addition an empty can is provided for use when measuring uranium materials of unknown ^{235}U abundances. SRM 969 was prepared as a set to permit measurement of materials containing uranium by using the theoretically expected linear relationship between ^{235}U abundance and the counting rate of the 185.7 keV gamma-ray of ^{235}U. Each SRM subunit is made up of 200 g of U_3O_8 powder. Since SRM 969 consists of 5 different containers, and each is unique in dimensions, the attached data sheets should be used with the specified container number. Individual data sheets are provided for each set of SRM's along with the certificate.

The certified $^{235}U/U$ isotope abundances are shown in Table 1. The isotope abundances for $^{234}U/U$, $^{236}U/U$, and $^{238}U/U$ are given in Table 2.

Table 1

Certified $^{235}U/U$ Abundances in SRM 969

Material ID:	031	071	194	295	446
Atom Percent:	0.3206 ±0.0002	0.7209 ±0.0005	1.9664 ±0.0014	2.9857 ±0.0021	4.5168 ±0.0032
Mass Percent	0.3166 ±0.0002	0.7119 ±0.0005	1.9420 ±0.0014	2.9492 ±0.0021	4.4623 ±0.0032

Statement of Uncertainty

The overall uncertainty of the $^{235}U/U$ abundance of each individual reference sample was estimated by combining the different uncertainty components from the mass spectrometry measurements and the $^{235}U/U$ homogeneity. The resulting values were conservatively enlarged to 0.07% to include other possible measurement errors.

Isotope Certification: The uranium isotopic abundances were determined by thermal ionization mass spectrometry (ThIMS) at the National Bureau of Standards (NBS) and by uranium hexafluoride mass spectrometry (UF_6 MS) and ThIMS at the Central Bureau of Nuclear Measurements (CBNM). These measurements were corrected for mass discrimination effects relative to NBS uranium isotopic SRM's or synthetic isotope mixtures.

Additional measurements supporting the certification were made by the U.S. Department of Energy, New Brunswick Laboratory (NBL), using ThIMS and by NBS using gamma spectrometry (see summary of the final results in Table 3).

Measurements by Gamma Spectrometry: The isotope abundance measurements and verification by gamma spectrometry were performed at NBS and CBNM utilizing the 185.7 keV gamma-ray of ^{235}U. All measurements were made using a high-resolution germanium detector. The heterogeneity of the $^{235}U/U$ in each SRM subunit is $\leq 0.05\%$ relative.

Gaithersburg, MD 20899
October 15, 1985
(Revision of Certificate
dated 6-27-85)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

Table 2. ^{234}U/U, ^{236}U/U and ^{238}U/U,
Abundances in SRM 969

Material	Uranium Isotopes		
	^{234}U/U	^{236}U/U	^{238}U/U
031 atom	0.0020	0.0147	99.6627
2s	±0.0002	±0.0003	± 0.0004
mass	0.0020	0.0146	99.6668
071 atom	0.0053	<0.00002	99.2738
2s	±0.0002		± 0.0004
mass	0.0052	<0.00002	99.2828
194 atom	0.0174	0.0003	98.0159
2s	±0.0002	±0.0001	± 0.0018
mass	0.0171	0.0003	98.0406
295 atom	0.0284	0.0033	96.9826
2s	±0.0004	±0.0002	± 0.0029
mass	0.0279	0.0033	97.0196
446 atom	0.0365	0.0069	95.4398
2s	±0.0003	±0.0002	± 0.0032
mass	0.0359	0.0068	95.4950

Measurements leading to the development and certification of this SRM were made at NBS in the Inorganic Analytical Research Division by B.S. Carpenter, J.W. Gramlich, R.R. Greenberg, and L.A. Machlan; at CBNM by E. Bouwmeester, R. Damen, P. De Bièvre, W. De Bolle, H.L. Eschbach, R. Eyckens, M. Gallet, W. Lycke, H. Meyer, G. Müschenborn, W. Nagel, F. Quik, and J. Van Audenhove; at U.S. Department of Energy New Brunswick Laboratory (NBL). by V.E. Connolly and A.C. Zook in the Safeguards Assessment and Reference Materials Branch.

The sampling plan used for the certification measurements was developed by W. Liggett, NBS Center for Applied Mathematics. The statistical assessment of the data used for the certification of this SRM was performed by R. Werz, CBNM.

The overall scope and coordination of the technical measurements leading to certification were performed by B.S. Carpenter, NBS, and P. De Bièvre, CBNM.

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

Supplemental Information

Description of SRM 969

The uranium oxides used for this SRM are from the same lots of material used and jointly certified by CBNM and NBS to produce this SRM and the Certified Nuclear Reference Material (EC NRM 171) for the Commission of European Communities.

For unique identification and for checking the integrity of the subunit, the plugs used for sealing the cans are equipped with ultrasonic seals, each having a unique ultrasonic spectrum.

Parameters that are of special interest for abundance measurements by gamma spectrometry are summarized below:

Chemical Purity of the U_3O_8

Material:	U_3O_8 powder
Total impurities:	<0.05 mass% of U_3O_8 content
Moisture content:	<0.3 mass% of U_3O_8 content

Uranium Minor Isotopes (that could interfere with gamma spectrometry measurements)

(Note: Data is presented as a ratio of the mass of the minor isotope to the mass of ^{235}U.)

Material ID	$^{232}U/^{235}U$	$^{233}U/^{235}U$	$(^{237}U + {}^{237}Np)/^{235}U$	Chemical Separation Date
031	$8x10^{-10}$	$<5x10^{-5}$	$<3x10^{-6}$	1977
071	$<0.3x10^{-10}$	$<5x10^{-5}$	$<3x10^{-6}$	1977
194	$0.3x10^{-10}$	$<5x10^{-5}$	$<3.10^{-6}$	1977
295	$0.1x10^{-10}$	$<5x10^{-5}$	$<3x10^{-6}$	1977
446	$1x10^{-10}$	$<5x10^{-5}$	$<3x10^{-6}$	1979

U_3O_8 Filling Information

Material ID	Mass (g)	Filling Height (mm)	Diameter (mm)	U_3O_8 Density (g/cm^2)
031	200.1 ±0.2	20.8 ± 0.5	70.00	5.2 ± 0.3
071	200.1 ±0.2	20.8 ± 0.5	70.00	5.2 ± 0.3
194	200.1 ±0.2	20.8 ± 0.5	70.00	5.2 ± 0.3
295	200.1 ±0.2	20.8 ± 0.5	70.00	5.2 ± 0.3
446	200.1 ±0.2	15.8 ± 0.5	70.00	5.2 ± 0.3

Container Material Characteristics and Specifications

Container Material:	Aluminum type 6061 (ASTM-GS T6) (All containers manufactured from the same base material)		
Constituent Elements: (in Base Material, Wt.%)	Mg 0.8 - 1.2	Zn ≤0.25	U ≤0.00025
	Si 0.4 - 0.8	Ti ≤0.15	Mn ≤0.15
	Cu 0.15 - 0.4	Fe ≤0.7	
	Cr 0.04 - 0.35	Total other Elements <0.15	

Container dimensions: See attached specifications

Use of SRM 969

Ideally, physical materials used for the evaluation of nondestructive measurements should be representative of the unknown samples with respect to all parameters that influence the measurement. One of the most crucial factors in gamma spectrometry is the strong attenuation of the gamma ray in the sample material itself and in the sample container. This attenuation is generally influenced by parameters such as sample size, shape, material density, and matrix composition. In addition, characteristics such as container material, wall thicknesses and container size can also influence attenuation.

SRM 969 is ideally suited for use with U_3O_8 materials contained in aluminum cans with 2mm bottom wall thickness. To be useful in the calibration of assay systems using other types of uranium samples, correction factors are needed. These factors are intended to normalize the gamma-ray response with respect to differences in both the matrix composition and the container. Typical correction factors are given in a special user's manual (Report KfK 3752(1984)) that has been prepared to facilitate the correct use of SRM 969 and EC NRM 171. Note: The attenuation correction factors given are based on theoretical values for photon cross sections. They represent a possible source of systematic error for those cases where the required corrections are large. Therefore, the correction given and the range of application should be experimentally validated to eliminate possible systematic errors from the gamma spectrometry abundance measurements.

Because the enrichment meter principle is based on the assumption that a sample is "quasi-infinitely thick" for the 185.7 keV gamma ray, the application of the method is inherently restricted to relatively large samples. About 200 g of unknown material is required when standard containers, with 7cm diameter, are used. For many applications it may be desirable to have reference samples that both physically and chemically differ from SRM 969. These reference samples can be calibrated against SRM 969.

Notice and Warnings

Container: The aluminum cans for SRM 969 have numbers engraved in the cylindrical wall. The numbering system on each can reflects the nominal isotope abundance of ^{235}U in mass percent and a sequence number. The cans within a set should have the same sequence number.

SRM 969 should be handled with great care to avoid any damage or deformation to the bottoms of the cans, since the bottoms serve as a window for the emitted gamma radiation. A special transport and storage case is supplied with this SRM.

Identification: A unique tamperproof system, making use of an ultrasonic "fingerprint" identification device, has been placed into the plug of each can.

Documentation

An NBS Special Publication, 260-96, and a European Commission Publication COM 4153, have been issued describing the preparation and characterization of this SRM, and should be used in conjunction with SRM 969/EC NRM 171. An additional User's Guide has been prepared and published as report KfK 3752.

Storage

The SRM subunits should be stored above −10 °C and below 40 °C.

Table 3. Summary of ^{235}U/U Isotope Abundance Measurements, in atom percent with 2s uncertainties, by Method and Laboratory

Material ID Laboratory/Method	031	071	194	295	446
CBNM-UF6	0.32049 ±0.00016	0.72096 ±0.00017	1.96575 ±0.00037	2.98432 ±0.00048	4.51668 ±0.00075
CBNM-ThIMS	0.32061 ±0.00047	0.72119 ±0.00098	1.9675 ±0.0017	2.9875 ±0.0039	4.5201 ±0.0052
NBS-ThIMS	0.32076 ±0.00052	0.72069 ±0.00068	1.9664 ±0.0017	2.9869 ±0.0022	4.5138 ±0.0033
NBL-ThIMS	0.3203 ±0.0007	0.7207 ±0.0007	1.9657 ±0.0015	2.9843 ±0.0039	4.5162 ±0.0039
NBS-Gamma	0.32053 ±0.00026	0.72081 ±0.00058	1.9660 ±0.0016	2.9830 ±0.0024	4.5158 ±0.0036