Commission of the European Communities

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^{235}Uranium isotope abundance certified reference material for gamma spectrometry

EC nuclear reference material 171 certification report

Report

EUR 10503 EN

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P. de Bièvre [1], H.L. Eschbach [1], R. Lesser [1]
H. Meyer [1], J. van Audenhove [1], B.S. Carpenter [2]

[1] Central Bureau for Nuclear Measurements
CEC — Joint Research Centre
B-2440 Geel

[2] National Bureau of Standards
Gaithersburg, Maryland, USA

Directorate-General Science, Research and Development
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^{235}URANIUM ISOTOPE ABUNDANCE CERTIFIED REFERENCE MATERIAL

FOR GAMMA SPECTROMETRY - EC NRM 171

Certification Report

1. Introduction

For the determination of isotope abundances with a small and specified uncertainty, calibration by isotope abundance certified reference materials is required.

The traditional technique for uranium isotope abundance measurements is the destructive assay (DA) of uranium materials by mass spectrometry. Related reference materials are characterized with the use of synthetic mixtures of enriched isotopes.

For non-destructive assay (NDA), reference materials must take the form of well specified physical samples for which not only the isotope abundances themselves must be known with sufficiently high accuracy but also all other specifications which may influence the property used to measure the isotope abundance like the counting rate of the ^{235}U characteristic gamma line at 185.7 keV.

The determination of the ^{235}U isotope abundance of uranium materials by non-destructive assay methods has found increased applications during recent years, for the following reasons:

- the advantage of NDA to perform in-field measurements and evaluation of results
- the small uncertainty achievable by gamma spectrometry when using high resolution Ge detectors.

High accuracy and the timeliness of results for the determination of the fissile material content are of special interest for safeguards purposes. In consequence, the ESARDA ★ Working Group on Techniques and Standards for Non-Destructive Analysis (ESARDA NDA WG) has formulated recommendations for the establishment of appropriate certified reference materials for the determination of the ^{235}U abundance of homogeneous uranium bulk materials.

★ European Safeguards Research and Development Association

A historical outline of these efforts was given at the 6th ESARDA Symposium (1). It was proposed to apply the enrichment meter principle (2) for which samples must take the form of chemically and isotopically homogeneous uranium layers which are preferably of ⩾ "99.9 % infinite thickness" for the most intense characteristic gamma-line of ^{235}U at 185.7 keV. If measured under well defined conditions, the counting rate at this energy is an accurate measure of the ^{235}U abundance, especially if high resolution (Ge) detectors are used for gamma spectrometry.

The reference materials described here have been prepared in a cooperative effort between the Central Bureau for Nuclear Measurements (CBNM) Geel and the National Bureau of Standards (NBS) Gaithersburg MD (3), in the framework of their respective Reference Material Programmes. Both CBNM and NBS are making them available as certified reference materials: EC NRM 171 and NBS SRM 969. They offer for the first time a possibility for a direct calibration of ^{235}U isotope abundance measurements by gamma spectrometry. It is part of the CBNM-NBS agreement that the final certified values must be the same in both certificates, however the further content and the format of the certification documents could be different.

This certification report describes mainly CBNM efforts and some NBS contributions. It presents also common CBNM-NBS certified values for the ^{235}U abundances and how these values have been obtained. The corresponding NBS report is NBS Special Publication 260-96 (22).

In Europe the certification of the reference materials was supported by a working group set up by CBNM according to an established procedure for the EC certification of nuclear reference materials. The working group was composed of European experts who have advised CBNM during the finalization of the certification report before it was passed to the EC Nuclear Certification Group.

A representative from NBS participated in one of the working group meetings as well as an observer from IAEA. The Euratom Safeguards Directorate has cooperated in the project.

A Users' Manual has been prepared by experts from Kernforschungszentrum Karlsruhe, FRG, on behalf of the ESARDA NDA WG (4).

A draft certificate for EC NRM 171 is enclosed as Appendix A and is in fact a summary of this certification report.

2. Description and intended use

The reference material consists of sets of five uranium oxide (U_3O_8) samples in cylindrical aluminium cans, with isotope abundances $^{235}U/U$ = 0.003; 0.007; 0.019; 0.029 and 0.045 (see Fig. 2-1). 50 sets each of these reference samples are available each in Europe from CBNM and in the USA from NBS. A reserve of 40 sets has been manufactured in order to cover additional needs in the future and is stored at CBNM. Each can contains 200 g U_3O_8 as a pressed powder layer with a diameter of 70 mm. In consequence a mean U_3O_8 surface density of 5.2 g cm^{-2} (measured parallel to the cylinder axis) was achieved, corresponding to a sample height of 2.0 cm for the majority of samples - for those with a ^{235}U abundance of 0.045 the sample height is 1.5 cm in order to ensure a stable material distribution within samples (see p. 12).

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" (the carefully controlled flat bottom), is about 99.9 % of the emission rate that can be obtained from an infinitely thick sample. The radiation is normally detected by a high-resolution gamma-detector for which a defined viewing angle is chosen by using a suitable Pb collimator (see Fig. 2-2).

The primary application of the reference samples as certified reference material is to perform accurate and internationally accepted calibrations of ^{235}U isotope abundance measurements on uranium samples or layers. Well defined measurement conditions are required for such calibrations since both the measurement on the material with an unknown abundance and on the reference sample must be performed with the same detector/collimator configuration. Additional requirements are the use of sufficiently thick and large as well as chemically pure uranium bearing material layers which are homogeneous with respect to their ^{235}U abundance and chemical composition as explained in some detail in the Users' Manual (4).

The unknown abundance (A_X) of a uranium material is obtained from gamma-counting and from the abundance (A_R) of a reference material by using the following formula * :

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* The linearity and zero intercept of the calibration curve for the measuring system used should have been confirmed by test measurements on a set of reference samples.

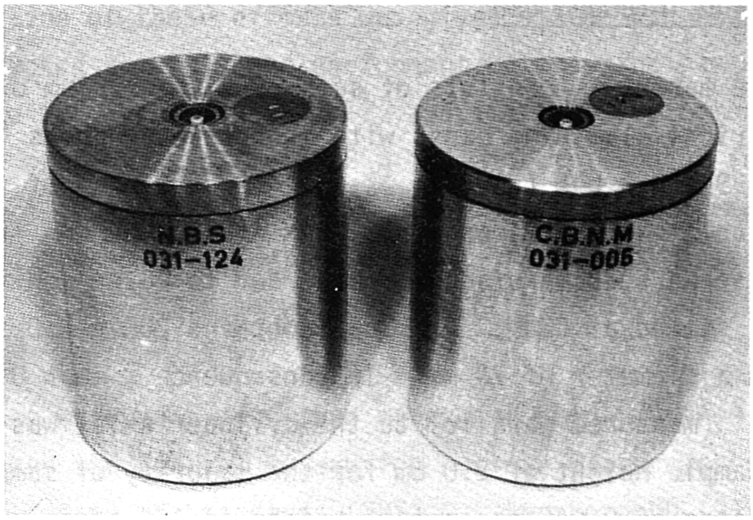


Fig. 2-1: ^{235}Uranium isotope abundance certified reference material samples for NDA-gamma spectrometry

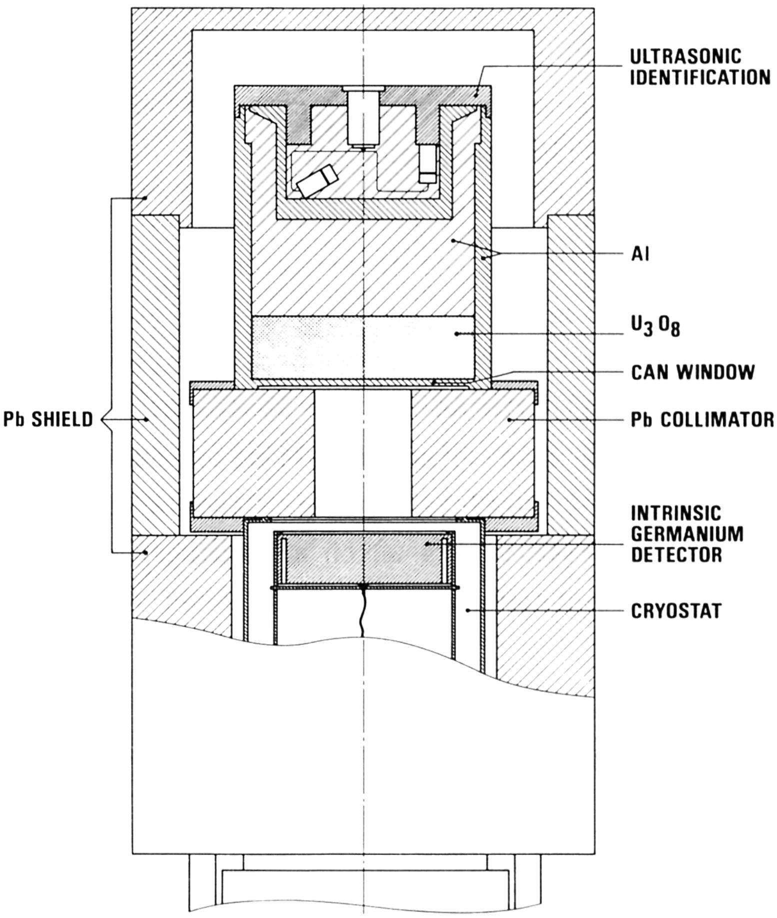


Fig. 2-2: Set-up for gamma spectrometry of U_3O_8 reference samples

$$A_X = A_R \frac{(K_\gamma C)_X}{(K_\gamma C)_R} K_m \cdot K_s \cdot K_c \qquad [2.1]$$

C_X, C_R are the peak counting rates for the 185.7 keV line determined from the gamma-spectra of both the unknown and of the reference samples (see typical spectra in Fig. 2-3).

$K_{\gamma X}$, $K_{\gamma R}$ are small corrections of peak counting rates for almost unresolvable gamma-lines near 185.7 keV from the protactinium daughter products of ^{238}U (5, 6);

$$(K_\gamma)_X = 1 - \Delta/A_X, \ (K_\gamma)_R = 1 - \Delta/A_R; \qquad [2.2]$$

where $\Delta \leqslant 1.15 \cdot 10^{-5}$ is in direct proportion to the fraction of those two protactinium gamma lines (^{234m}Pa at 184.7 keV, ^{234}Pa at 186.0 keV) which are evaluated as part of the peak counting rate of the 185.7 keV line of ^{235}U (for uranium more than 100 days after chemical purification (4)).

K_m, K_s, K_c are to correct for differences between unknown and reference materials with respect to material and sample properties.

K_m is related to the chemical composition of the uranium materials.

K_s is related to the surface density of the uranium samples compared to "infinite thickness".

K_c is related to the material type and thickness of the can "windows".

An empty aluminium can, identical to the ones used for the reference samples is supplied together with each set of reference materials for facilitating the measurement of unknown materials. When this can is used K_c becomes equal to one.

For identification of the reference samples, numbers are engraved in the wall of the cans as shown in Fig. 2-1. The numbers give the issuing organization, i.e. CBNM or NBS, a three digit number for the $^{235}U/U$ abundances (in mass per cent) and a three digit sequential number common to all samples of a set (see chapter 4).

For ultrasonic identification all samples are equipped with a unique and tamper proof system consisting of a seal inserted into the top part of the can. For identification a special ultrasonic transceiver is available which can read the ultrasonic fingerprint in the seal via the connector on the cover of the cans (see also refs. 4, 7). In such a way a verification of the signature of a sample is possible.

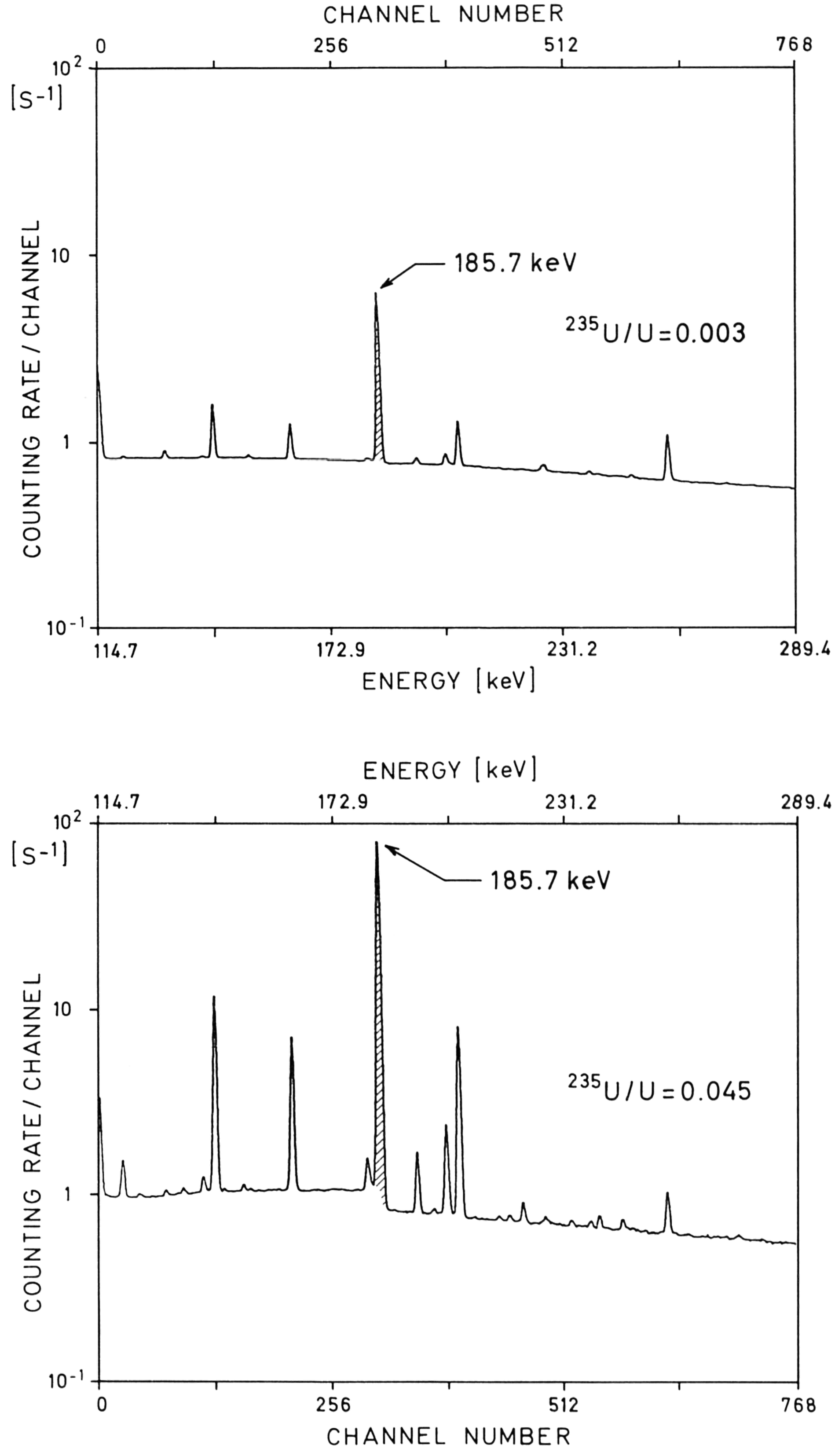


Fig. 2-3: Gamma-spectra of U_3O_8 reference samples measured with a high resolution germanium detector

3. Quantities to be certified and specified

The aim of this reference material project was to make available reference samples with characteristics enabling highly accurate $^{235}U/U$ abundance determinations to be made by high resolution gamma spectrometry. A total uncertainty of 0.25 % or better at the 95 % confidence level was considered to fulfil existing needs for most applications and to correspond to the state of the art of gamma spectrometry.

There are a number of properties of the reference samples the uncertainty of which contribute to the total uncertainty of the emission rate of the 185.7 keV photons used as a measure of the ^{235}U abundance; these are:

- the ^{235}U abundances of the U_3O_8 materials and their isotopic homogeneity,
- the chemical purity and homogeneity of the U_3O_8 materials,
- the surface density and consequently the degree of infinite thickness of the U_3O_8 samples,
- the thickness of the container windows,
- gamma emitting impurities from uranium isotopes and their daughter products.

$^{235}U/U$ abundances (certified)

The nominal values of the five different abundances $^{235}U/U$ in mass are: 0.0031; 0.0071; 0.0194; 0.0295 and 0.0446. The material identification numbers (031, 071, 194, 295, 446) have been derived from these numbers. The accurate abundances have been determined as follows:

- by thermal ionization mass spectrometry; all measurements have been corrected for mass discrimination effects with the aid of synthetic mixtures of highly enriched ^{235}U and ^{238}U isotopes.
- by UF_6 gas mass spectrometry of the ratios $^{235}U/^{238}U$ against synthetic mixtures of highly enriched isotopes.

The isotopic homogeneity was tested by UF_6 gas mass spectrometry at CBNM on material samples taken before and during the preparation of the reference samples.

Common certified values on the certificates will be issued by CBNM and NBS.

Chemical and physical sample properties (specified)

Properties of the reference samples other than the ^{235}U abundance will affect the correction factors (K) in formula [2.1] and their uncertainties when a measurement on an unknown sample is calibrated by the use of reference samples.

Chemical composition and impurities (K_m). Material samples have been taken and analysed before and during the preparation of the reference samples in order to specify the deviation of chemical properties from pure U_3O_8.

U_3O_8 surface sample density (K_s). The degree of infinite thickness of the surface density of the reference samples has been tested by measuring the gamma counting rate of the 185.7 keV line of ^{235}U on samples with different thickness. The homogeneity of surface density of the reference samples was tested by gamma transmission measurements.

Container window material and thickness (K_c). The containers of the reference samples have been produced from one batch of aluminium. Consequently the window material of all reference samples is assumed to be identical. The window thickness of all reference samples has been tested by an ultrasonic thickness gauge.

Gamma emitting impurities from uranium isotopes other than ^{235}U and daugther products were investigated by checking the occurrence of gamma lines in the energy region around 185 keV.

Bias effects from gamma lines of ^{232}U, ^{233}U and ^{237}U and their daughter products can be expected, in addition to those from ^{238}U daughters, when measuring the ^{235}U characteristic gamma line with low resolution counters (NaI). ^{238}U daughter products will affect measurements mainly before the secular equilibrium of daughter production and decay is reached. Only ^{234}Pa lines from ^{238}U at 184.7 and 186.0 keV will also affect high-resolution gamma counting and corrections are required especially for low ^{235}U abundance materials (K_γ, see formula [2.2]).

4. Fabrication of the Reference Samples

The main steps in the fabrication are:

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

Emphasis was put on extensive control and inspection throughout the fabrication route to guarantee the required specifications.

4.1. Fabrication of cans and plugs

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

Dimensions and tolerances of can and plug are given in Fig. 4.1-1.

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

Si : 0.4 - 0.8
Fe : ≤ 0.7
Cu : 0.15 - 0.4
Mn : ≤ 0.15

Mg : 0.8 - 1.2
Cr : 0.04 - 0.35
Zn : ≤ 0.25
Ti : ≤ 0.15
U : ≤ 0.000 25 [★]

Other elements : each ≤ 0.05
: total ≤ 0.15

All metrological data are listed on a sheet, as shown in Fig. 4.1-2 provided with each reference material container. The measurement of can window thicknesses as well as the selection of cans are described in section 8.4.

[★] 2.5 µg/g Uranium in the can material will affect gamma measurements by less than 3 parts per 10^6 (for measurements on uranium with $^{235}U/U \geq 0.3$ %); this was verified experimentally with an uncertainty of 10 parts per 10^6 by gamma measurements on an empty can.

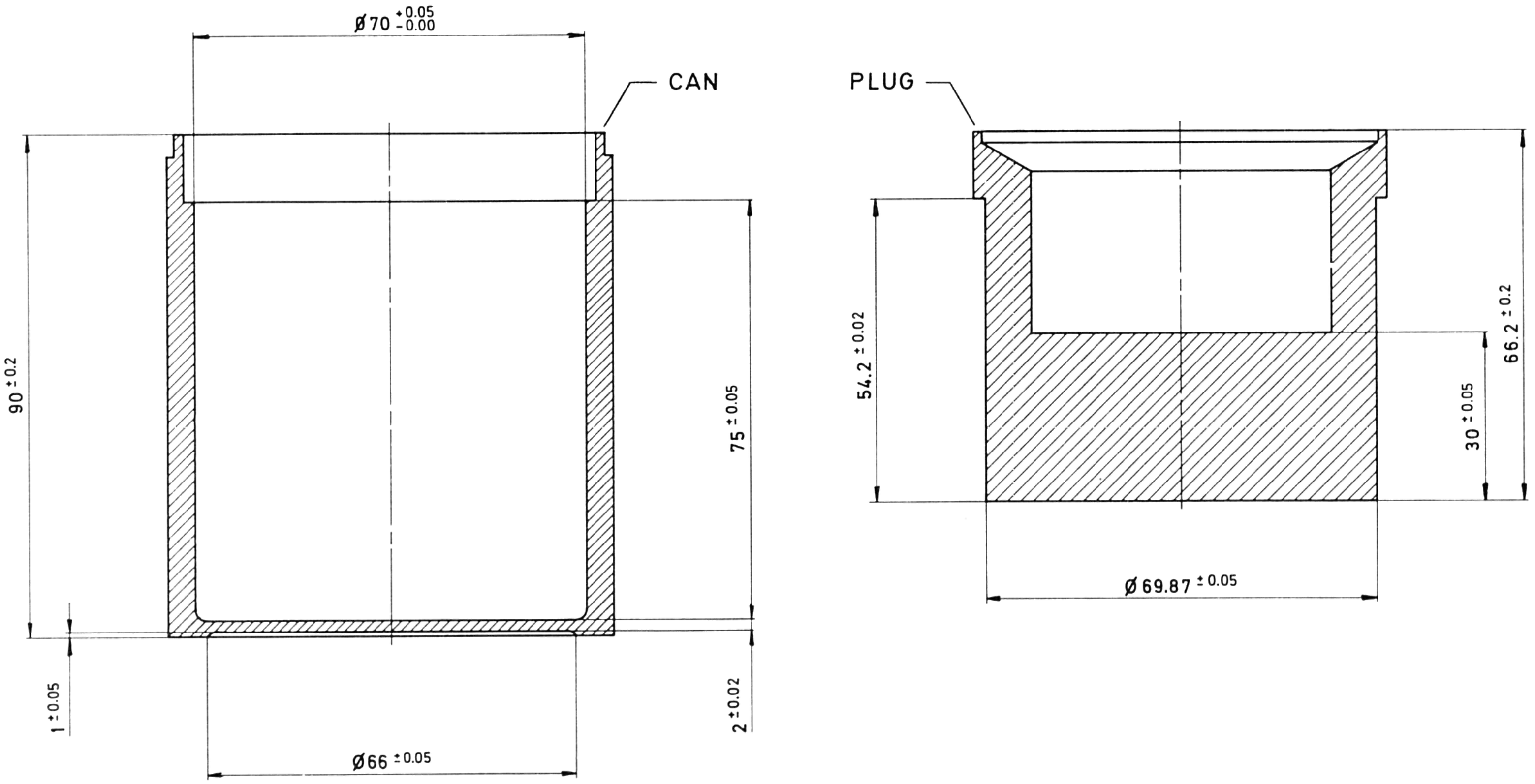


Fig. 4.1-1 Dimensions and tolerances of the U_3O_8 NDA RM cans. Material: Al-alloy ASTM 6061-T6 (all dimensions in mm)

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
h	87.00
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
	$\bar{s}_{13}$	0.009 (all areas)
	$\bar{x}_5$	1.989
	$\bar{s}_5$	0.010 (five inner areas)

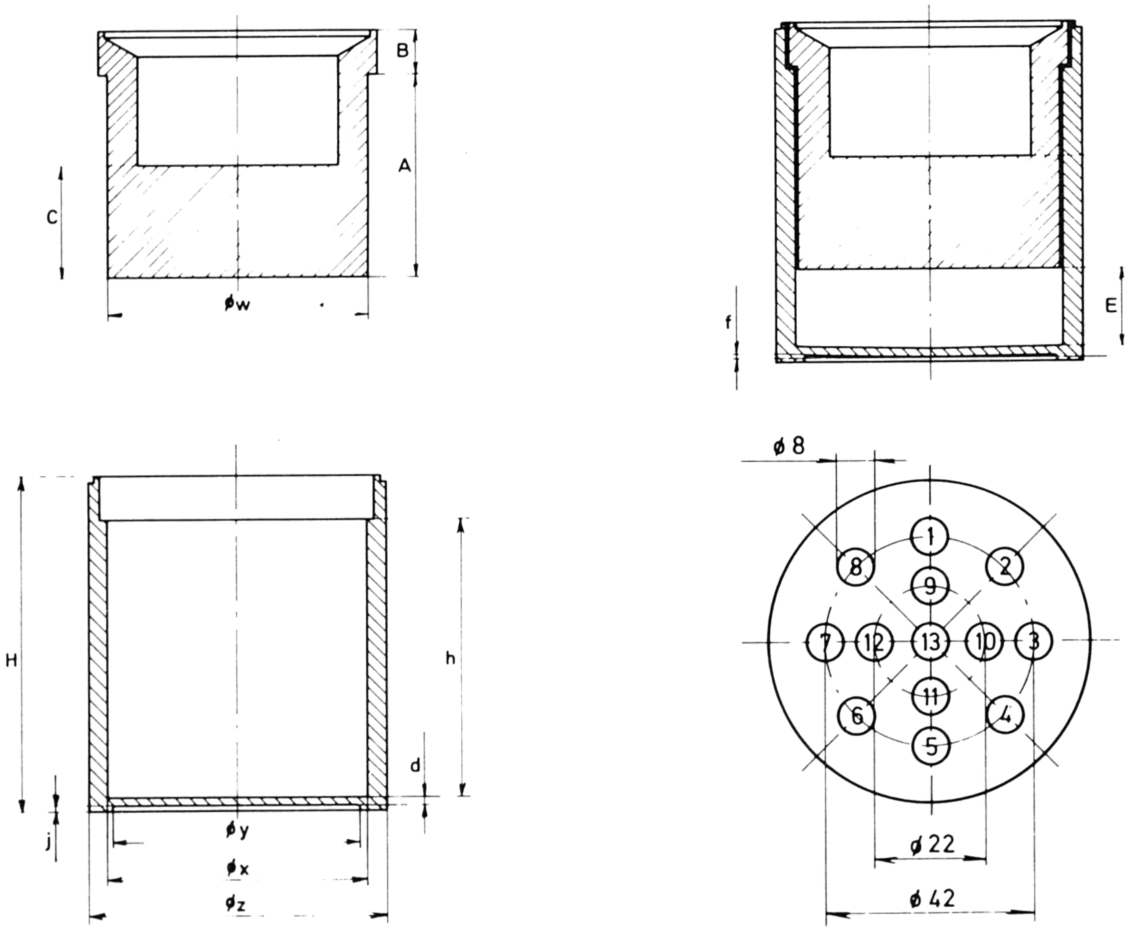


Fig. 4.1-2 Example of dimensional control of can and window (all dimensions in mm)

4.2. Filling of the U_3O_8 powder into the cans

The required amount of (200 ± 0.2) g of U_3O_8 (surface density: 5.2 $g.cm^{-2}$) was weighed in the can and pressed 3 mm above the required final thickness by means of a steel plug on a hydraulic press (diameter of steel plug = 69 mm, inner diameter of can = 70 mm so that air could escape during pressing).

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 and determined again. This preliminary pressing was performed twice. With the hydraulic press the permanent Al-plug was then placed into its final position such that the lips of plug and can were pressed together. In order 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 on a Mettler balance type PC 2000 with a weighing range of 2100 g, a reproducibility of ± 0.01 g and a linearity of ± 0.015 g. This balance has been calibrated every day with a test weight calibrated against the CBNM standard kilogramme (8). The indicated uncertainty of ± 0.2 g on the U_3O_8 mass is a maximum.

Four U_3O_8 materials (031, 071, 194, 295) had pour densities of 0.7 to 0.9 $g.cm^{-3}$ and were pressed in the cans to a density of about 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, did show that this material still moved within the can when pressed to a density of about 2.5 $g.cm^{-3}$ and caused an unacceptable reduction of the U_3O_8 layer at distinct surface areas within the can. Repressing 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. This was confirmed by gamma-transmission measurements.

The lips of the plugs and the cans 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.

The external dimensions were checked again after complete fabrication and the window flatness of the can corrected, if needed, by pressing on a suitable convex or concave base plate.

Numbers were engraved in the top part of the cylindrical wall of the cans as shown in Fig. 2-1.

The numbering system was chosen as follows:

- The reference samples distributed by CBNM and NBS respectively for e.g. the $^{235}U/U$ = 0.0031 material indicate the abundance as "031", and a sequential set number of 001 through 070 for CBNM and 071 through 140 for NBS cans e.g.

CBNM 031-001 (set 001) or CBNM 031-015 (set 015)
NBS 031-071 (set 071) or NBS 031-086 (set 086)

- Reference samples with the same sequential number (001; 071; 015; 086 in the examples) form a set of RM's. The empty can, provided in addition, has the corresponding sequential number as shown in examples of the numbering system:

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

4.3. Sampling for filling procedure and homogeneity verification

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 10 can fillings. These samples were used for chemical impurity and moisture determinations as well as for checking isotopic homogeneity (see sections 5.4.3 and 8.1).

4.4. Ultrasonic identification system

Special attention was given to the unique ultrasonic identification system of each of the reference samples, as described in (7).

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

- an ultrasonic transducer identifies uniquely the box and is embodied in the structure thus making tampering difficult (identifier)
- an 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 Fig. 4.4-1a) for easy identity and integrity check by simple electric connection of an ultrasonic reader (e.g.: a commercially available portable apparatus SONIC MK 1/EURATOM modification).

Recording of the identity can be performed using a simple polaroid camera to print the pattern appearing on the screen of the portable reader (see Fig. 4.4-1b). This pattern of the ultrasonic spectrum is specific to each can.

The identifier and integrity verifier will demonstrate changes of pattern of the ultrasonic spectrum to detect any tampering to the can.

The EURATOM Safeguards Directorate, Luxembourg, has registered the ultrasonic pattern of each seal.

Storage temperatures between -10 and +40°C are preferred in order not to destroy the seals.

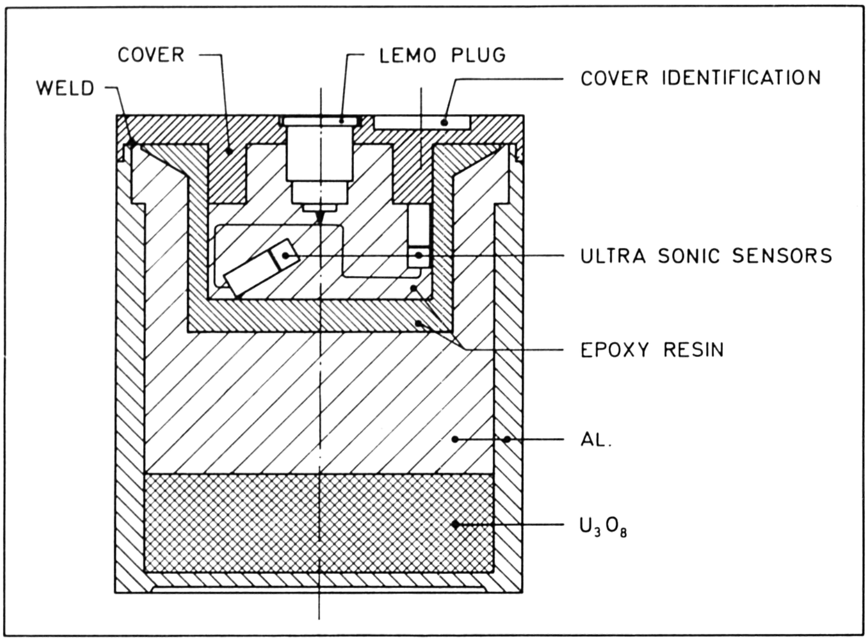


Fig. 4.4-1a. Ultrasonic sensors as integrated part of reference samples

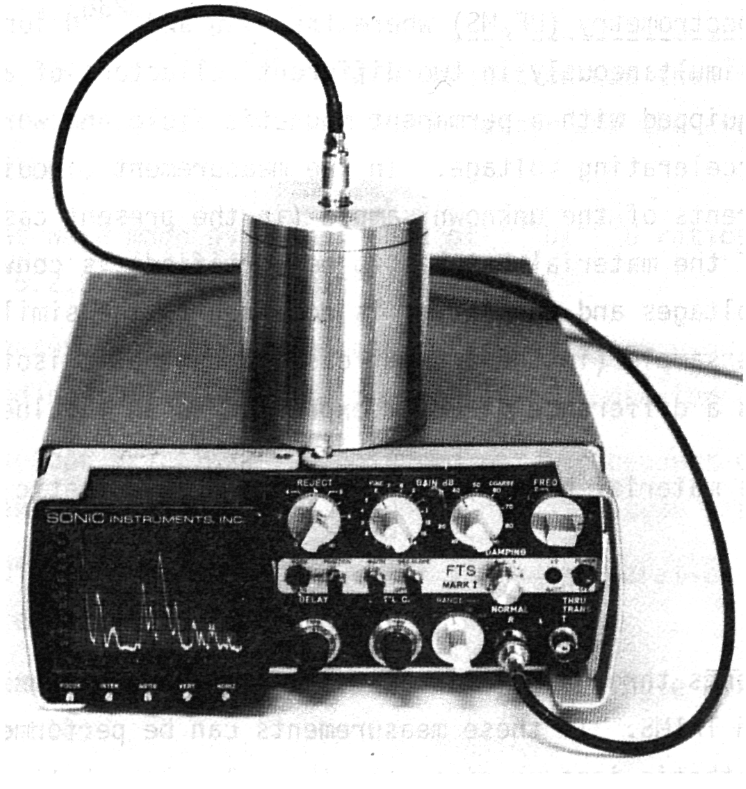


Fig. 4.4-1b. Registration of the specific ultrasonic pattern of each can

Fig. 4.4-1. Transducer system for the ultrasonic identification of the reference samples

5. Characterization of the Abundances ^{235}U/U at CBNM

^{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:

- 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:

  $$(^{235}\mathrm{U}/^{238}\mathrm{U})\ \text{material batch} = \mathbf{K}_{5/8} \cdot (^{235}\mathrm{U}/^{238}\mathrm{U})\ \text{measured} \qquad [5b]$$

  where $\mathbf{K}$ is a correction factor for systematic errors.

- UF$_6$ 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 at a constant accelerating voltage. In the measurement circuitry the ratio of ion currents of the unknown sample (in the present case: a sample from one of the material batches to be certified) is converted into a ratio of voltages and the latter is compared to the similar ratio of a reference sample (in the present case: a synthetic isotope mixture). This yields a difference directly expressed as an α-value. Hence

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

  or

  $$R_{\mathrm{m.b.}} = \alpha \cdot R_{\mathrm{s.m.}} \qquad [5c]$$

  α-measurements through UF$_6$ mass spectrometry have better reproducibility than ThIMS. If these measurements can be performed directly against synthetic isotope mixtures, they also have better accuracy.

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

Calibration of the measurements

All measurements were carried out after all precautions had been taken to correct or eliminate known systematic errors of instrumental nature.

Correction for additional systematic errors as well as mass discrimination in the ion sources will be considered separately for ThIMS and UF_6MS.

a) Thermal ionization mass spectrometry

Corrections from unknown sources of systematic error as well as 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, known 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 permits the detection, quantification and correction for isotope fractionation by means of the correction factor $\mathbb{K} = R_{prep}/R_{obs}$.

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

The mixtures were made over the range of $^{235}U/^{238}U$ ratios concerned (see Table 5.2.2.1a) and demonstrated that:

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

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

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

(4) a contamination in the preparation of any single mixture was not detectable.

This approach has been used previously to produce Isotopic Reference Materials for boron (9) and lithium (10,11).

Since isotope fractionation, as determined over 3 mass units difference (235-238), was only 0.03 % (see Section 5.2.2.1) 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.

b) UF_6 Mass Spectrometry

Corrections from unknown sources of systematic error 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, known from their preparation to 0.01 % and prepared to match the isotopic composition of the material batches (i.e. the candidate RM's) to within 1 %.

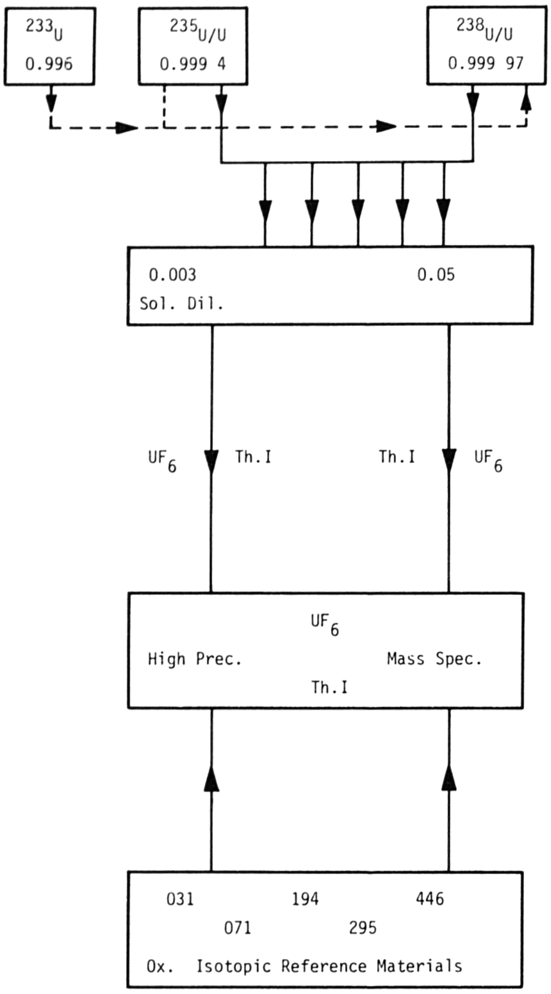
The chemical conversion of the mixtures to UF_6 normally requires 2-3 g material per sample. It was obviously impossible to consume that large an amount of enriched isotopes per mixture. The entire procedure was therefore miniaturized until chemical conversions on a 100 mg scale could be achieved without loss of accuracy (12,13).

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

The working scheme which has been followed is illustrated schematically in Fig. 5. The different parts of it will be described:

- the preparation of the synthetic mixtures and their uncertainty components (Section 5.1)
- the mass spectrometric measurements and their calibration (Section 5.2)
- computing the $^{235}U/U$ abundances and their uncertainties (Section 5.3).

In the discussion of a particular 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, then the uncertainty of the correction factor(s) incorporated in the uncertainty of that particular measurement and this combined uncertainty transferred to the next step of the process. All experimental uncertainties will be expressed as 2s (s = standard deviation of the single determination). This corresponds 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 the squares (independent determinations) except when indicated otherwise. This was the case when calculating the uncertainty on $^{235}U/U$ abundances (Eq. [5.5.2]).



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

Fig. 5.: Scheme for the preparation of synthetic isotope mixtures in order to put "absolute" values (with uncertainties) on Isotopic Reference Materials

5.1. Preparation of synthetic uranium isotope mixtures

Enriched isotopes were purified chemically and converted to the highly stable U_3O_8 (see 5.1.2). On a weight basis they were mixed to achieve different isotope ratio values (see Table 5.1.4) in the range 0.003-0.05 corresponding to $^{235}U/U$ abundances 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 isotopes
- corrections for water uptake and the weighing of the enriched isotope oxide fractions
- dissolution of the weighed fractions.

5.1.1. Isotopic purity of the highly enriched isotopes

Table 5.1.1. gives the results of the measurements.

atom abundances	enriched ^{235}U	enriched ^{238}U
^{233}U/U	< 0.000 000 2 ★	< 0.000 000 2 ★
^{234}U/U	0.000 360 7 2 6	0.000 000 3 2
^{235}U/U	0.999 414 5 6 0	0.000 023 4 4
^{236}U/U	0.000 095 3 5 2	< 0.000 000 1 ★
^{238}U/U	0.000 129 5 1 5	0.999 976 3 4

Table 5.1.1.: Isotope abundances of enriched isotope materials used to prepare the synthetic isotope mixtures.
Uncertainties (indicated under the values) are 2s slightly enlarged to take into account max. possible effects of slight irregularities in the background of the mass spectrum

★ Detection limits; these values are not considered to be real isotopic abundances.

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 "internal isotopic standard" (see upper part of Fig. 5).

This was particularly important for the measurement of the ^{235}U abundance in the ^{238}U enriched material since the accuracy of the $^{235}U/^{238}U$ ratio in the mixtures is dominated by the accuracy of the ^{235}U abundance in the ^{238}U enriched material (14). This material was spiked with CBNM Isotope Reference Material 040-1 (^{233}U) (15) to give a 235/233 ratio approximately equal to one and this ratio was measured. The $^{235}U/^{238}U$ ratio was then determined as $^{235}U/^{238}U = {}^{235}U/^{233}U \cdot N_{233}/N_{238}$ where N_{233} is the number of ^{233}U atoms added. Both N_{233} and N_{238} were determined from weighing the calcined oxide and correcting for oxygen content and isotopic purity.

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

In arriving at the final abundances and uncertainties shown in Table 5.1.1, all possible sources of error were considered since the uncertainty of the enriched isotopes constitutes an important component of the total uncertainty of the mixtures (see Table 5.1.4).

The following sources of error were evaluated:

- Interference from unresolved molecular species: the spectrum was closely examined using the highest sensitivity available and because this contribution depended 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 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 are required. The isotope most affected was the ^{236}U in the ^{235}U-enriched material where it was necessary to allow for a 3.0 % (2s) uncertainty.

5.1.2. 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 are a sufficient requirement. Chemical purification of the two enriched isotopes was therefore carried out using the same procedures. The isotopes were purified by cation exchange on Dowex 50 X 8 (100-200 mesh, H-form) resin with a 90 % tetrahydrofuran/10 % 6 M HNO_3 solution as eluent, followed by calcination at 900°C for 3 hours. The U_3O_8 was redissolved in 6 M 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 $\mu g.g^{-1}$ impurities) and 99.99 % (about 100 $\mu g.g^{-1}$ impurities) after purification (see Table 5.1.2).

The purity check was made with the aid of a JEOL-01-BM-2 double focusing spark source mass spectrometer (SSMS) and using Relative Sensitivity Factors (RSF) 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.

In order to account for possible undetected impurities, (200 ± 100) $\mu g.g^{-1}$, instead of 100 $\mu g.g^{-1}$ 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 are given in Table 5.1.4.

	blanco $\mu g.g^{-1}$		^{235}U ($\mu g.g^{-1}$)				^{238}U ($\mu g.g^{-1}$)			
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
Ti	-	< 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 $\leqslant 1\ \mu g.g^{-1}$)

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

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

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

$$+ 2\ NO_3^{-} \xrightarrow{900°C} \cdot\ U_3O_8 .$$

(3) after peroxide precipitation (Au-matrix)

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

(4) after peroxide precipitation (C-matrix)

Table 5.1.2.: Spark Source Mass Spectrometric Analysis of the enriched ^{235}U and ^{238}U isotopes used in the preparation of the mixtures

5.1.3. 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 only an identical composition, not necessarily theoretical (i.e. stoichiometrical), is needed. Moreover, U_3O_8 is known to be reproducible to $\leqslant 0.01$ % in composition when calcined for a minimum of 1 hour at 900°C.

Both enriched isotope oxides were calcined simultaneously in two quartz tubes during 16 h at 900°C in a furnace having a temperature uniformity of $\pm$ 2.5°C and a difference between two quartz tubes of 1°C max. at the 900°C equilibrium situation. This step eliminated volatile impurities.

The calcination was performed under an air flow of about 7 ml per minute on portions of about 1 g. Subsequently the crucibles were cooled down on a large aluminium block and weighed after 24 hours. Another 2 h calcination followed and the process was repeated until the mass differences were less than 20 μg (possible error $<$ 20 ppm and hence negligible). All operations were performed in a glove-box with a controlled humidity of 10-50 μg water g^{-1} dry air. Water uptake proved to be $<$ 5 μg on 1 g samples (possible error $<$ 5 ppm and hence negligible) during the weighing periods of 1 h maximum. Weighing uncertainty was $\leqslant$ 5 μg in all cases.

At this point in the operations, samples were taken to determine the isotopic compositions given in Table 5.1.1.

5.1.4. Isotope mixtures and their uncertainties

Under the above described conditions, a series of synthetic isotope oxide mixtures was prepared by weight and the values calculated from the preparation ("R_{prep}"). These values are given in Table 5.1.4 with their uncertainties $2s_R$ 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 weights calibrated against the CBNM standard kilogramme (8). The latter is calibrated directly against the standard kilogramme of the Bureau International des Poids et Mesures in Sèvres.

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 $R_{prep} + 2s_R$		isotopic purity	stoichi-ometry	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 5.1.4.: Prepared isotope mixtures, with uncertainties (2s) and their components: 100 parts in 10^6 = 0.01 %

The $^{235}U/^{238}U$ ratio $R_{5/8}$ in the mixture is obtained from the $^{235}U/^{238}U$ ratios R in the enriched isotope materials A (enriched ^{235}U) and B (enriched ^{238}U) as follows:

$$R_{5/8} = \frac{R_A(1 + R_B)N_A/N_B + R_B(1 + R_A)}{(1 + R_B)N_A/N_B + (1 + R_A)} \qquad |5.1.4.a|$$

where N is the number of atoms of uranium element in the enriched materials. The actual relation used is much more complicated because it accounts for masses instead of numbers of atoms, correction factors for chemical purities, oxygen excess in the oxides and different atomic weights of the uranium.

Uncertainties on $R_{5/8}$ were calculated by proper propagation of error of Eq. [5.1.4.a] including partial derivation with respect to all relevant variables. These calculations are very complicated if carried out to the full extent and will be reported elsewhere (20). The results are summarized in Table 5.1.4.

5.2. Mass spectrometric measurements and their calibration

5.2.1. UF_6 Mass Spectrometry

Samples of the material batches and synthetic mixtures were converted to UF_6 according to a standard procedure (12). For each isotopic composition, two synthetic mixtures were prepared "bracketing" the material batch nominal value to within 1 %. $^{235}U/^{238}U$ values for the material batches were then determined by performing one α-measurement series against each of the mixtures, thus yielding two values (see Eq. [5c]). Results are given in Table 5.2.1.

5.2.2. Thermal Ionization Mass Spectrometry

5.2.2.1. $^{235}U/^{238}U$ ratio determinations

The synthetic mixtures prepared were made up to the required concentrations, measured on the mass spectrometer and corrected for known (instrumental) bias, yielding observed values R_{obs}. Remaining unknown systematic biases (mostly from isotope fractionation in the ion source) were quantified and an appropriate correction factor, κ, determined as

$$\kappa = \frac{R_{prep}}{R_{obs}}$$

The results of this first series of ThIMS measurements are given in Table 5.2.2.1.a .

The resulting correction factor, κ, 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".

Material	Synthetic Mixture Used		UF$_6$ α-measurement	"absolute" atom $^{235}U/^{238}U$ value on material batch as determined by	
	Identi-fication	preparation value		"single standard" method	"double standard" method
031	82	0.003 210 19 41	1.001 71 56	0.003 215 7 1 9	0.003 215 7 1 6
	83	0.003 241 59 41	0.992 13 52	0.003 216 1 1 7	
071	118	0.007 206 69 61	1.007 75 31	0.007 262 5 2 3	0.007 262 3 1 7
	119	0.007 326 01 62	0.991 27 31	0.007 262 0 2 3	
194	102	0.020 183 6 1 8	0.993 58 24	0.020 054 0 5 2	0.020 055 2 3 8
	103	0.019 976 7 2 1	1.003 97 24	0.020 055 9 5 3	
295	104	0.030 599 0 3 2	1.005 60 21	0.030 770 4 7 3	0.030 771 1 5 1
	105	0.030 982 0 3 2	0.993 22 20	0.030 772 0 6 8	
446	106	0.047 121 6 4 7	1.004 34 21	0.047 326 11	0.047 324 8 8 2
	107	0.047 546 7 4 8	0.995 30 25	0.047 323 13	

Table 5.2.1.: Determination of $^{235}U/^{238}U$ ratios against synthetic isotope mixtures by UF$_6$ MS
Uncertainties indicated under the values are 2s (n = 12)
The last column contains the result of the "double standard" method i.e., an interpolation of the measurement between the two measurements against the two synthetic mixtures

$^{235}U/^{238}U$ mixtures			correction factor K
Ident. No.	$R_{preparation}$	$R_{observed}$	$= \frac{R_{preparation}}{R_{observed}}$
82	0.003 210 19 41	0.003 213 3 2 4	0.999 0
83	0.003 241 59 41	0.003 242 0 3 2	0.999 9
84	0.007 238 63 56	0.007 241 9 5 4	0.999 6
85	0.007 302 88 57	0.007 306 8 3 4	0.999 5
102	0.020 183 6 1 8	0.020 186 10	0.999 9
103	0.019 976 7 2 1	0.019 987 10	0.999 5
104	0.030 599 0 3 2	0.030 606 4	0.999 8
105	0.030 982 0 3 2	0.030 990 11	0.999 7
106	0.047 121 6 4 7	0.047 137 32	0.999 7
107	0.047 546 7 4 8	0.047 529 26	1.000 4
			0.999 7 2s = ± 0.000 7 (n = 10)

Table 5.2.2.1.a.: ThIMS measurements: (1st series): correction factor, K, determined with synthetic isotope mixtures over an R range 0.003 - 0.05. Uncertainties indicated are 2s.
(In view of the uncertainties in the R_{obs}-values, the small trend in the K-values is insignificant).

The correction factor, **K**, for all remaining systematic errors, mainly isotope fractionation is

$$\mathbb{K} = 0.999\,7 \pm 0.000\,7 \qquad (2s,\ n = 10)$$

This correction factor, **K**, was applied to all $^{235}U/^{238}U$ thermal ionization measurements shown in Table 5.2.2.1.b (see below). A correction factor per mass unit was calculated as $1 - \frac{1-0.999\,7}{3}$ and **K** factors derived for the other ratios:

	K	Isotope effect (%)
for $^{235}U/^{238}U$ (3 mass units)	0.999 7	0.03
for $^{234}U/^{238}U$ (4 mass units)	0.999 6	0.04
for $^{236}U/^{238}U$ (2 mass units)	0.999 8	0.02

Material batch	atom $^{235}U/^{238}U$ ratios observed	correction factor **K**	atom $^{235}U/^{238}U$ ratios corrected
031	0.003 220 3 4 0	0.999 7 7	0.003 219 3 4 6
071	0.007 270 4 5 7	0.999 7 7	0.007 268 2 7 7
194	0.020 090 16	0.999 7 7	0.020 084 21
295	0.030 830 33	0.999 7 7	0.030 821 39
446	0.047 405 39	0.999 7 7	0.047 391 51

Table 5.2.2.1.b.: Observed and corrected atom $^{235}U/^{238}U$ ratios for ThIMS (1st series). Uncertainties indicated are 2s (n = 6)

The unsatisfactory agreement between the UF_6MS and the ThIMS values (1st series), led to a second series of ThIMS measurements, using the same synthetic mixtures, but a different mass spectrometer and analyst. The resulting **K** factors are given in Table 5.2.2.1.c, the observed and corrected $^{235}U/^{238}U$ atom ratios are given in Table 5.2.2.1.d. In Table 5.2.2.1.e all the CBNM mass spectrometry measurements are summarized.

$^{235}U/^{238}U$ mixtures			correction factor K $= \frac{R_{preparation}}{R_{observed}}$
Identification No.	$R_{preparation}$	$R_{observed}$	
82	0.003 210 19 41	0.003 215 6 2 7	0.998 32 (n = 5) 84
85	0.007 302 88 57	0.007 317 7 8 6	0.997 97 (n = 6) 1 12
102	0.020 183 6 1 8	0.020 217 (n = 3) 5	0.998 32 (n = 6) 39
103	0.019 976 7 2 1	0.020 011 (n = 3) 12	
104	0.030 599 0 3 2	0.030 638 (n = 2) 45	0.998 75 (n = 5) 96
105	0.030 982 0 3 2	0.031 020 (n = 3) 28	
106	0.047 121 6 4 7	0.047 219 (n = 3) 57	0.997 88 (n = 6) 80
107	0.047 546 7 4 8	0.047 650 (n = 3) 8	

Table 5.2.2.1.c.: ThIMS measurements (second series): correction factor K determined with synthetic isotope mixtures over an R range 0.003 - 0.05. Uncertainties indicated are 2s

Material batch	$^{235}U/^{238}U$ atom ratios observed	correction factor K	$^{235}U/^{238}U$ atom ratios corrected
031	0.003 220 2 4 0	0.998 32 84	0.003 214 6 4 9
071	0.007 276 9	0.997 97 1 12	0.007 261 2 12 2
194	0.020 097 12	0.998 32 39	0.020 063 15
295	0.030 827 31	0.998 75 96	0.030 788 44
446	0.047 434 50	0.997 88 80	0.047.333 63

Table 5.2.2.1.d.: ThIMS observed and corrected atom $^{235}U/^{238}U$ ratios (second series). Uncertainties indicates are 2s (n = 12)

Material	$^{235}U/^{238}U$ atom ratios			
	UF_6MS	ThIMS		
		first series	second series	average
031	0.003 215 7 1 6	0.003 219 3 4 6	0.003 214 6 4 9	0.003 217 0 4 8
071	0.007 262 3 1 7	0.007 268 2 7 7	0.007 261 2 12 2	0.007 265 2 10 0
194	0.020 055 2 3 8	0.020 084 21	0.020 063 15	0.020 074 18
295	0.030 771 1 5 1	0.030 821 39	0.030 788 44	0.030 805 42
446	0.047 324 8 8 2	0.047 391 51	0.047 333 63	0.047 362 57

Table 5.2.2.1.e.: $^{235}U/^{238}U$ atom ratio values as determined by ThIMS and UF_6MS. Uncertainties indicated are 2s and do contain the uncertainties of the measurements as well as on the synthetic mixtures

5.2.2.2. Determination of the Minor Isotope Abundances

These abundances were measured relative to the 235 isotope, using an electron multiplier. With the aid of the ^{235}U/^{238}U ratio values, they were converted in ratios relative to ^{238}U e.g. $^{234}\mathrm{U}/^{235}\mathrm{U} \cdot {}^{235}\mathrm{U}/^{238}\mathrm{U} = {}^{234}\mathrm{U}/^{238}\mathrm{U}$.

An upper limit for the abundance of ^{233}U was estimated in 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 in Section 5.1.1. 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 5.2.2.2 below.

Material	^{234}U/^{238}U atomic isotope ratio	^{236}U/^{238}U atomic isotope ratio
031	0.000 020 2 1 2	0.000 146 5 8 6
071	0.000 052 8 3 1	< 0.000 000 2
194	0.000 176 10	0.000 002 86 53
295	0.000 289 16	0.000 033 6 2 4
446	0.000 38 2	0.000 072 4

Table 5.2.2.2.: ^{234}U/^{238}U and ^{236}U/^{238}U ratio determinations by ThIMS
Uncertainties indicated are 2s (n = 6)

5.3. Computing ^{235}U/U abundance values

In Table 5.2.2.1.e. the $^{235}U/^{238}U$ ratios obtained from UF_6MS and ThIMS are compared.

The average isotope ratios given in Tables 5.2.2.2 and 5.2.2.1.e. have been used to derive the ^{235}U/U abundances according to Eq. [5a] and these are given in Table 5.3.1.

The 2s uncertainties given include those from the mass spectrometric measurements and from the isotope mixture preparation process.

The ^{234}U/U, ^{236}U/U and ^{238}U/U abundances are given in Tables 5.3.2 to 5.3.4.

For the conversion from atom abundances to mass abundances, the following atomic masses were used (16):

234.040 947 4 ± 0.000 005 2
235.043 925 2 ± 0.000 005 2
236.045 562 9 ± 0.000 005 0
238.050 785 8 ± 0.000 004 8

Material	^{235}U/U	
	atom abundance from UF_6MS	atom abundance from ThIMS
031	0.003 204 9 1 6	0.003 206 1 4 7
071	0.007 209 6 1 7	0.007 211 9 9 8
194	0.019 657 5 3 7	0.019 675 0 17 3
295	0.029 843 2 4 8	0.029 874 6 39 0
446	0.045 166 8 7 5	0.045 200 7 51 9

Table 5.3.1.: ^{235}U/U abundances from UF_6MS and ThIMS
Uncertainties indicated are 2s

Material	$^{234}U/U$		
	atom abundance	mass abundance	uncertainty (2s)
031	0.000 020 1	0.000 019 8	± 0.000 001 2
071	0.000 052 4	0.000 051 5	± 0.000 003 0
194	0.000 172 4	0.000 169 5	± 0.000 010 2
295	0.000 279 9	0.000 275 3	± 0.000 015 9
446	0.000 363 6	0.000 357 6	± 0.000 020 8

Table 5.3.2.: Abundances $^{234}U/U$
Uncertainties indicated are 2s

Material	$^{236}U/U$		
	atom abundance	mass abundance	uncertainty (2s)
031	0.000 146 0	0.000 144 8	± 0.000 009 0
071	< 0.000 000 2	< 0.000 000 2	-
194	0.000 002 8	0.000 002 8	± 0.000 000 5
295	0.000 032 6	0.000 032 3	± 0.000 002 3
446	0.000 068 7	0.000 068 2	± 0.000 004 2

Table 5.3.3.: Abundances $^{236}U/U$
Uncertainties indicated are 2s

Material	$^{238}U/U$		
	atom abundance	mass abundance	uncertainty (2s)
031	0.996 629 0	0.996 670 9	0.000 009 1
071	0.992 737 9	0.992 829 2	0.000 003 5
194	0.980 167 3	0.980 413 7	0.000 010 7
295	0.969 844 3	0.970 214 9	0.000 016 5
446	0.954 400 9	0.954 952 1	0.000 021 3

Table 5.3.4.: Abundances $^{238}U/U$
Uncertainties indicated are 2s

5.4. Isotopic homogeneity

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

- by imposing requirements on the supplier's chemical preparation process
- by measuring the isotopic composition of the samples taken from the batches as delivered (13 samples)
- by measuring the isotopic composition of samples taken during the can filling process.

Also the γ measurements described under section 8.6 may be considered as a verification of isotopic homogeneity.

The chemical preparation and the sampling procedure of the materials are summarized in Fig. 5.4.

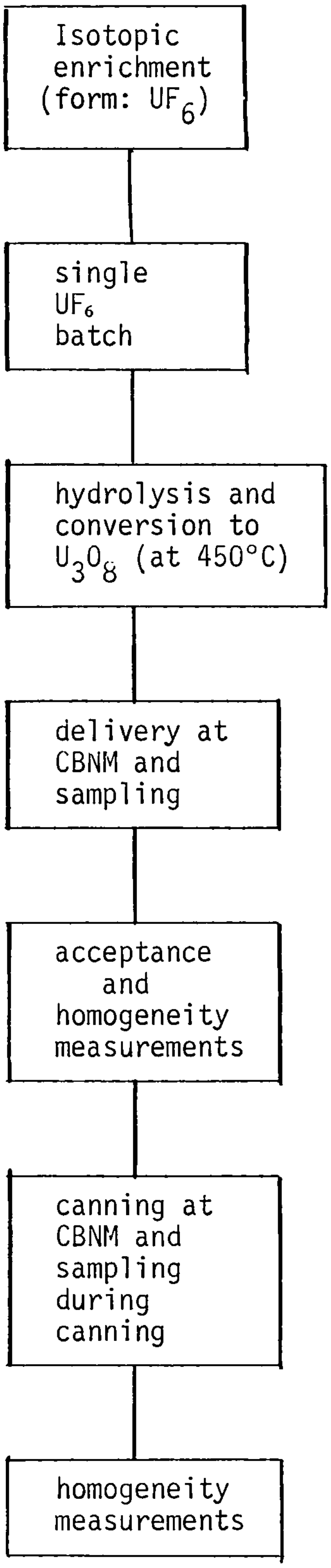
5.4.1. Requirements on the supplier's chemical preparation process

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 passed the stage of being handled as one single lot in one container in order to let the material isotopically homogenize in the UF_6 gas/liquid phase. Subsequent hydrolysis and calcination to 450°C was performed in clean installations, one batch at a time, rigorously isolated from any other material (17).

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 from powder mixing (17).

5.4.2. Upon delivery at CBNM

Each batch was sampled at 12 different positions according to a well-defined scheme given in Fig. 5.4.2-1: 4 samples from the top part, 4 samples from the middle part and 4 from the bottom part of each batch. A 13th sample, taken at random, (in the Fig. sample "33") served as the tie-point for the relative measurements. The Figure also indicates the sample sizes taken, as well as the identification numbers of all samples in each batch.



- each material (except natural U) was taken from the enrichment plant as one single batch
- natural U was directly converted to UF_6

- each batch was processed in a single lot and stored in a 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 30kg for isotopic homogeneity checks

- relative measurements 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

Fig. 5.4.: Homogeneity verification of materials

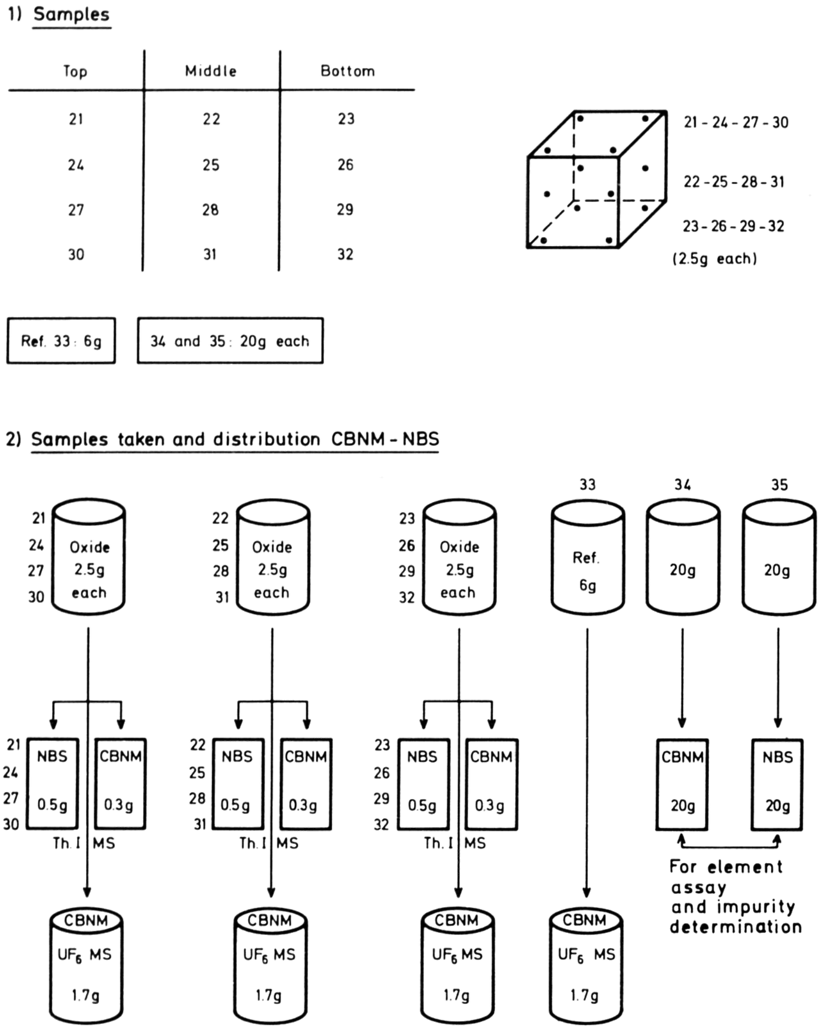


Fig. 5.4.2-1.: Sampling of U_3O_8 NDA RM batches for isotopic measurements (example: material 071)

A check of isotopic homogeneity was then carried out by UF_6 gas mass spectrometry: after conversion to UF_6 (12), 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 (18). Particular attention was given to the UF_6 sample vessels to ensure that there was no cross-contamination (19).

The results of checking isotopic homogeneity of each material batch upon delivery are given in Table 5.4.2-1. These measurements have been considered as acceptance measurements on the material as received and have not been taken into account in the uncertainty of the final certified abundances.

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 % on the 031 material batch is caused by two of the 12 samples which show a deviation of about 0.06 % in their $^{235}U/^{238}U$ ratios.

Material	$a = \dfrac{(^{235}U/^{238}U)_{sample}}{(^{235}U/^{238}U)_{sample\ 33}}$	uncertainty (2s)	2s in %
031	1.000 14	± 0.000 54 (n = 12)	0.054
071	0.999 88	± 0.000 11 (n = 12)	0.011
194	0.999 92	± 0.000 18 (n = 12)	0.018
295	1.000 00	± 0.000 15 (n = 12)	0.015
446	0.999 98	± 0.000 12 (n = 12)	0.012

Table 5.4.2.1.: Check of isotopic homogeneity by UF_6 MS of the base materials upon acceptance. Uncertainties are 2s. Measurements performed on 12 samples vs a 13th sample (sample "33" for material 071) taken at random

5.4.3. During the process of filling the Al containers

About 15 samples for each material 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_6 gas mass spectrometry. An example is given in Table 5.4.3.1. for one material (the natural uranium 071); the random sample used as reference in this case is sample "33" which is the same sample as mentioned in Section 5.4.2.

Results for all materials are summarized in Table 5.4.3.2. On the basis of 0.5 g samples the isotopic homogeneity of the materials is confirmed to within 0.025 %. The values for the 031 material do include one result for a sample which deviated 0.04 % from the others.

Sample number	$a = \frac{^{235}U/^{238}U \text{ sample}}{^{235}U/^{238}U \text{ sample "33"}}$	2s (n = 24)
21p *	1.000 11	± 0.000 34
22p	0.999 96	± 0.000 36
23p	1.000 09	± 0.000 37
24p	1.000 05	± 0.000 34
25p	1.000 04	± 0.000 35
26p	1.000 14	± 0.000 35
27p	1.000 17	± 0.000 30
28p	1.000 08	± 0.000 39
29p	1.000 04	± 0.000 34
30p	1.000 14	± 0.000 36
31p	1.000 11	± 0.000 36
32p	0.999 99	± 0.000 34
33p	1.000 08	± 0.000 34
34p	1.000 02	± 0.000 34
35p	0.999 99	± 0.000 34
36p	1.000 03	± 0.000 36
37p	1.000 11	± 0.000 38
38p	0.999 94	± 0.000 46
Average	1.000 06	± 0.000 12 (0.012 %) (2s, n = 18)

Table 5.4.3.1.: Check of isotopic homogeneity by UF_6 Mass Spectrometry during filling for the 071 material
Uncertainties indicated are 2s

* "p" indicates samples taken during the can filling process as opposed to those taken before (Table 5.4.2.1)

Material	α measured	uncertainty (2s)
031	1.000 24	0.000 23 (n = 8)
071	1.000 06	0.000 13 (n = 18)
194	1.000 06	0.000 14 (n = 7)
295	1.000 05	0.000 06 (n = 8)
446	1.000 01	0.000 12 (n = 6)

Table 5.4.3.2.: UF_6 MS check of isotopic homogeneity during filling of the cans on the basis of 0.5 g samples

5.5. Evaluation of the overall uncertainty of the $^{235}U/U$ abundances

For this evaluation Eq. [5a]

$$^{235}U/U = \frac{^{235}U/^{238}U}{^{234}U/^{238}U + {}^{235}U/^{238}U + {}^{236}U/^{238}U + 1}$$

is written as

$$A_5 = \frac{R_5}{R_4 + R_5 + R_6 + 1} \qquad [5.5.1]$$

$$= \frac{R_5}{N}$$

In order to calculate the 1s-uncertainty on the abundance A_5, the following quantities are needed: the 1s-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 to calculate the 1s-uncertainty on A_5 from Eq. [5.5.1] as follows:

$$s^2(A_5) = \frac{s_2^2 - 2A_5(\sum_i s_2 s_i \cdot \rho_{2i}) + A_5^2 \sum_{i,j} s_i \cdot s_j \cdot \rho_{ij}}{(R_4 + R_5 + R_6 + 1)^2} \qquad [5.5.2]$$

where $i,j = 1, 2, 3$ and

$$s_1 = s(R_4), \quad s_2 = s(R_5), \quad s_3 = s(R_6)$$

$$\rho_{11} = \rho_{22} = \rho_{33} = 1 \qquad [5.5.3]$$

$$\rho_{12} = \rho(R_4,R_5), \quad \rho_{13} = \rho(R_4,R_6), \quad \rho_{23} = \rho(R_5,R_6)$$

$$A_5 = {}^{235}U/U$$

Using ratios and their 1s-values derived from Tables 5.2.2.1.e and 5.2.2.2 values for $s(A_5)$ were obtained as given in Table 5.3.1.

In the present case the terms s_i, s_j, ρ_{ij} with $i = j$ were important ($\rho_{ij} = 1$), but terms with $i \neq j$ were extremely small because at least one factor of the term, either s_i, s_j or ρ_{ij} was very small. This was due to the fact that $^{235}U/^{238}U$ ratios were measured independently by UF_6 MS from the $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios by ThIMS.

All uncertainty 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 5.5.2 (20).

uncertainty source \ material	031	071	194	295	446
1. preparation synthetic mixtures (from Table 5.1.4)					
- isot. purity	113	51	21	16	13
- stoichiometry	44	44	45	45	44
- chem. purity	14	14	14	14	14
- weighing	34	49	89	92	88
2. UF_6 α-measurements (calculated from Table 5.2.1)	467	210	160	126	135
3. $^{234}U/^{238}U$ measurements (from Table 5.2.2.2, and Eq. [5.5.2])	1	3	10	16	21
4. $^{236}U/^{238}U$ measurements (from Table 5.2.2.2, and Eq. [5.5.2])	9	< 1	< 1	2	4
Sub-Total	484	227	190	165	170
5. Isotopic homogeneity (from Table 5.4.3.2)	230	130	140	60	120
Overall	536	262	236	176	208

Table 5.5.2.: Components of the uncertainty of the $^{235}U/U$ abundance determination and the verification of isotopic homogeneity (expressed in parts per 10^6 of value)

6. Characterization of the abundances $^{235}U/U$ at NBS

Details for this section are taken from NBS Special Publication 260-96 (22).

6.1. Sample preparation for the isotopic measurements

6.1.1. Materials 031, 194, 295 and 446 by the Uranyl Nitrate Dihydrate procedure

a. Filament material:

All analyses were performed using a rhenium triple filament ion source (23). 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 less stable signal with less internal precision than can be obtained with regular rhenium (24). Therefore, zone-refined rhenium is not recommended for this procedure. A U^+/UO^+ ratio of 10^3 or greater at 20 minutes in the analysis 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 1×10^{-4} 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 on 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 isotopic fractionation correction is very dependent on sample size (Fig. 6.1.1-1), the amount of uranium on the filament has to be very carefully controlled. Drying of the solution on 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 (25) which precisely controlled the current through the filaments, and the drying time. The uranium samples were dried under the following conditions: approximately 40°C for 10 minutes, approximately 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/minute). Different air flow rates require readjustment of the filament currents to maintain the proper temperature (Fig. 6.1.1-2). 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 the oxide.

The first step of the drying procedure deposits the uranium on the rhenium filaments as the 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 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 (26,27). 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 high precision 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 1×10^{-4} Pa, liquid nitrogen was added to the source cold trap to further reduce the pressure to 1×10^{-5} 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 1.0 A through the 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.

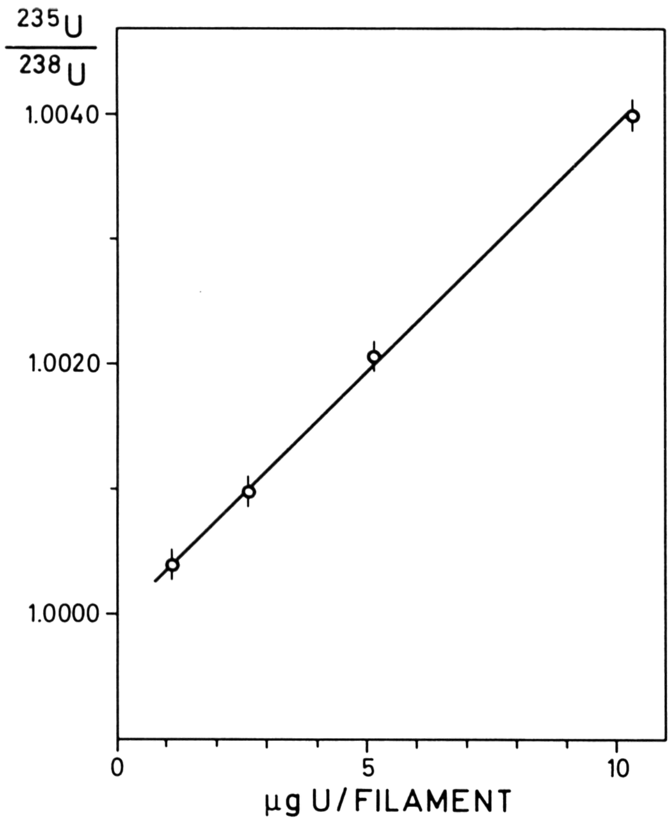


Fig. 6.1.1-1.: Observed $^{235}U/^{238}U$ ratio of SRM U-500 versus sample size

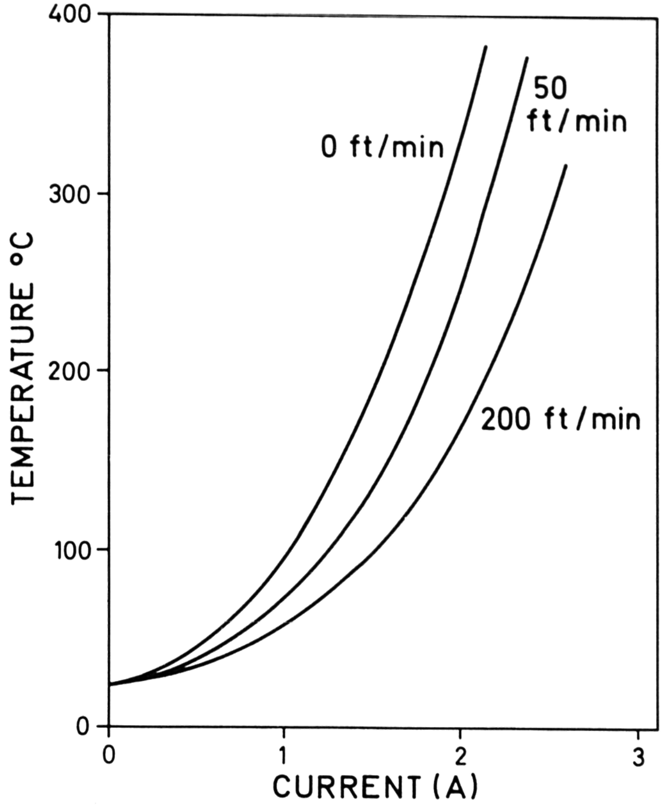


Fig. 6.1.1-2.: Effect of air flow on rhenium filament temperature

After the source pressure had returned to 1 x 10^{-5} 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 1.50 A. At 5 minutes into the analysis the sample filament currents were increased to produce a total uranium 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. 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 isotope fractionation. Observed isotope 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.

6.1.2. Material 071 by the UO_3 analysis procedure

Due to the recertification of several uranium isotopic Standard Reference Materials, synthetically prepared calibrated mixes were available for determining the isotope fractionation corrections for the 071 material. These calibration mixes were prepared from chemically and isotopically pure ^{238}U and ^{235}U solutions which were assayed prior to mixing by 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 analyses 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 (28). 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.

6.2. 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 multicomponent deep-bucket Faraday cage collector (29). 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.

6.3. Sampling scheme and preparation of synthetic uranium isotope mixtures

A sampling scheme for the characterization measurements as well as the verification of isotopic homogeneity was designed by the NBS Center for Applied Mathematics and supplied to CBNM for guidance during sampling and filling of the cans. 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 Fig. 5.4.2-1.

Approximately 3 mg of U_3O_8 were 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 1 mg 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 0.8 M 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 $\geqslant$ 0.005 percent. Features of this procedure have been adapted to the conditions of the standard NBL titration (approximately 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 (30). 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 found 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 sulphate is employed to reduce U(VI) to U(IV) in a concentrated phosphoric acid solution containing sulphamic acid. The excess ferrous ion is selectively oxidized by nitric acid in the presence of Mo(VI) as a catalyst. Cold water and vanadyl sulphate quench the oxidation and prepare the sample for titration. The U(VI) must be titrated within 2-3 minutes using standard SRM potassium dichromate and a potentiometric end point.

To improve titration precision, two weight burettes were used to dispense a concentrated and a dilute dichromate solution into the sample to potentials of approximately 480 and 550 mV, respectively. A very dilute dichromate solution was added in increments of 50 μl by a calibrated repeating pipette 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.

6.4. Mass spectrometric measurement results

All of NBS mass spectrometry results are given in Tables 6.4.1 - 6.4.5.

6.5. Uncertainties in the isotope ratios and abundances

The 1s uncertainties reported in Tables 6.4.1 - 6.4.5 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 Table 7.4 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 isotope ratio, B is the 2s uncertainty on the isotope 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 isotope correction factor. This term also includes components to cover the uncertainties in the isotope composition and assay of the separated isotopes used in the preparation of synthetic mixes. In all cases, the stated uncertainties reported in Tables 7.1 and 7.4 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.

Sample	238	236	235	234
1	99.662 28	0.014 684	0.321 033	0.002 006
2	99.662 50	0.014 810	0.320 705	0.001 982
3	99.662 28	0.014 863	0.320 881	0.001 977
4	99.662 70	0.014 740	0.320 575	0.001 984
5	99.662 91	0.014 555	0.320 530	0.002 004
6	99.662 24	0.014 772	0.321 005	0.001 987
7	99.662 50	0.014 693	0.320 808	0.002 002
8	99.662 92	0.014 558	0.320 536	0.001 984
9	99.662 60	0.014 906	0.320 501	0.001 994
10	99.662 75	0.014 755	0.320 492	0.001 999
11	99.661 97	0.014 817	0.321 208	0.002 004
12	99.662 35	0.014 822	0.320 832	0.001 999
Average atom %	99.662 50	0.014 748	0.320 759	0.001 994
Standard deviation	0.000 14	0.000 110	0.000 240	0.000 010
Average weight %	99.666 69	0.014 624	0.316 721	0.001 960
Atomic Weight = 238.0408				

Table 6.4.1.: NBS measured isotope abundances for the 031 material (atom percent)

Sample	238	235	234
22-1	99.274 21	0.720 50	0.005 29
22-2	99.273 92	0.720 77	0.005 31
22-3	99.273 84	0.720 79	0.005 36
22-4	99.273 91	0.720 80	0.005 29
27-col-1*	99.273 79	0.720 86	0.005 35
27-col-2	99.274 09	0.720 56	0.005 35
28	99.273 92	0.720 76	0.005 32
32	99.274 06	0.720 60	0.005 34
32-col-3	99.274 11	0.720 54	0.005 35
Average atom %	99.273 98	0.720 69	0.005 33
Standard deviation	0.000 14	0.000 14	0.000 03
Average weight %	99.283 11	0.711 65	0.005 24
Atomic Weight = 238.0289			

* Initial measurements on this material, using the uranyl nitrate dihydrate sample loading procedure, produced abnormal mass spectrometric behaviour, indicating possible interferences from chemical impurities. To insure that this problem would not bias the measurements using the UO$_3$ sample loading procedure, three samples (designed by -col) were further purified with an anion exchange column.

Table 6.4.2. NBS measured isotope abundances for the 071 material (atom percent)

Sample	238	236	235	234
41	98.015 38	0.000 31	1.966 51	0.017 80
42	98.015 38	0.000 31	1.966 64	0.017 66
43	98.015 73	0.000 29	1.966 47	0.017 50
44	98.015 72	0.000 29	1.966 41	0.017 58
45	98.015 29	0.000 33	1.966 74	0.017 64
46	98.015 78	0.000 31	1.966 29	0.017 62
47	98.015 58	0.000 33	1.966 44	0.017 64
48	98.016 20	0.000 29	1.965 95	0.017 55
49	98.015 42	0.000 30	1.966 56	0.017 72
50	98.015 31	0.000 35	1.966 48	0.017 85
51	98.015 79	0.000 28	1.966 06	0.017 87
52	98.016 19	0.000 31	1.965 67	0.017 83
Average atom %	98.015 65	0.000 31	1.966 35	0.017 69
Standard deviation	0.000 17	0.000 02	0.000 31	0.000 12
Average weight %	98.040 29	0.000 31	1.942 00	0.017 40
Atomic Weight = 237.9909				

Table 6.4.3.: NBS measured isotope abundances for the 194 material (atom percent)

Sample	238	236	235	234
61	96.981 13	0.003 23	2.986 70	0.028 94
62	96.980 67	0.003 29	2.987 15	0.028 88
63	96.981 54	0.003 43	2.986 21	0.028 82
64	96.979 45	0.003 20	2.988 17	0.028 68
65	96.980 58	0.003 32	2.987 25	0.028 86
66	96.980 82	0.003 32	2.986 89	0.028 97
67	96.981 02	0.003 26	2.987 05	0.028 67
68	96.981 27	0.003 26	2.986 71	0.028 76
69	96.981 53	0.003 23	2.986 67	0.028 58
70	96.981 40	0.003 32	2.986 38	0.028 91
71	96.981 51	0.003 29	2.986 36	0.028 85
72	96.981 45	0.003 26	2.986 75	0.028 55
Average atom %	96.981 03	0.003 28	2.986 86	0.028 79
Standard deviation	0.000 33	0.000 06	0.000 52	0.000 14
Average weight %	97.018 17	0.003 25	2.950 26	0.028 32
Atomic Weight = 237.9597				

Table 6.4.4.: NBS measured isotope abundances for the 295 material (atom percent)

Sample	238	236	235	234
81	95.441 99	0.006 95	4.514 35	0.036 70
82	95.441 30	0.007 00	4.514 64	0.037 07
83	95.443 02	0.006 99	4.512 89	0.037 10
84	95.444 00	0.006 95	4.512 48	0.036 55
85	95.441 90	0.007 00	4.514 18	0.036 92
86	95.443 59	0.006 95	4.512 57	0.036 73
87	95.442 35	0.006 95	4.514 18	0.036 52
88	95.442 92	0.006 95	4.513 39	0.036 74
89	95.441 73	0.006 95	4.514 34	0.036 97
90	95.442 22	0.006 95	4.514 13	0.036 70
91	95.442 01	0.006 91	4.514 20	0.036 88
92	95.442 06	0.006 70	4.514 42	0.036 52
Average atom %	95.442 42	0.006 94	4.513 81	0.036 78
Standard deviation	0.000 76	0.000 08	0.000 77	0.000 20
Average weight %	95.497 56	0.006 88	4.459 37	0.036 18
Atomic Weight = 237.9133				

Table 6.4.5.: NBS measured isotope abundances for the 446 material (atom percent)

7. Common CBNM-NBS values for certification

The $^{235}U/^{238}U$ ratios as measured by each mass spectrometry laboratory are given in Table 7.1. These measurements reflect both laboratory methods, thermal ionization mass spectrometry and UF_6 mass spectrometry. The values for the ^{234}U and ^{236}U isotope abundances were determined from the CBNM and NBS measurements by ThIMS only. These abundances are presented in Table 7.2, suggested common CBNM-NBS values of ^{234}U, ^{236}U and ^{238}U in Table 7.3.

As mentioned earlier, this certified reference material has been prepared in a cooperative effort between CBNM and NBS and is available as EC NRM 171 or NBS SRM 969. The certified $^{235}U/U$ abundance values are based on CBNM hexafluoride mass spectrometry (UF_6MS) and thermal ionization mass spectrometry (ThIMS), and on NBS thermal ionization mass spectrometry. In computing common certified values, a 1/1 weight was assigned to UF_6MS/ThIMS and also to CBNM ThIMS/NBS ThIMS. Hence the values are calculated according to:

$^{235}U/U$ abundance = (0.5· "UF_6MS") + (0.25· "CBNM ThIMS") + (0.25· "NBS ThIMS").

Material	Laboratory method		
	CBNM-UF_6	CBNM-ThIMS	NBS-ThIMS
031	0.321 57 16	0.321 70 48	0.321 84 52
071	0.726 23 17	0.726 52 1 00	0.725 96 68
194	2.005 52 38	2.007 4 1 8	2.006 2 1 7
295	3.077 11 51	3.080 5 4 2	3.079 8 2 2
446	4.732 48 82	4.736 2 5 7	4.729 4 3 3

Table 7.1.: $^{235}U/^{238}U$ mass spectrometry ratios with 2s uncertainties (percent)

Material		^{234}U (atom percent)	^{236}U (atom percent)	^{238}U (atom percent)	At. Wt.
031	CBNM-ThIMS	0.002 01 12	0.014 60 90	99.662 90 91	238.040 87
	NBS	0.001 994 20	0.014 748 220	99.662 50 28	238.040 8
071	CBNM-ThIMS	0.005 24 30	< 0.000 02	99.273 79 35	238.029 19
	NBS	0.005 33 6	0.000 00	99.273 98 28	238.028 9
194	CBNM-ThIMS	0.017 24 1 02	0.000 28 5	98.016 73 1 07	237.991 7
	NBS	0.017 69 24	0.000 31 4	98.015 65 34	237.990 9
295	CBNM-ThIMS	0.027 99 1 59	0.003 26 23	96.984 43 1 65	237.960 9
	NBS	0.028 686 104	0.003 28 12	96.981 03 66	237.959 7
446	CBNM-ThIMS	0.036 36 2 08	0.006 87 42	95.440 09 2 13	237.915 0
	NBS	0.036 78 40	0.006 94 16	95.442 42 1 52	237.913 3

Table 7.2.: Summary of uranium isotope abundance measurements by ThIMS for ^{234}U, ^{236}U, and ^{238}U (Uncertainties are 2s)

Material		Uranium isotopes		
		^{234}U	^{236}U	^{238}U
031	atom percent	0.002 0	0.014 7	99.662 7
	2s	2	3	4
	mass percent	0.002 0	0.014 6	99.666 8
071	atom percent	0.005 3	< 0.000 02	99.273 8
	2s	2		4
	mass percent	0.005 2	< 0.000 02	99.282 9
194	atom percent	0.017 4	0.000 3	98.015 9
	2s	2	1	1 8
	mass percent	0.017 1	0.000 3	98.040 6
295	atom percent	0.028 4	0.003 3	96.982 6
	2s	4	2	2 9
	mass percent	0.027 9	0.003 3	97.019 6
446	atom percent	0.036 5	0.006 9	95.439 8
	2s	3	2	3 2
	mass percent	0.035 9	0.006 8	95.495 0

Table 7.3.: Suggested common CBNM-NBS values of ^{234}U, ^{236}U and ^{238}U abundances

In Table 7.4 the results from this calculation are presented for the atom abundances, together with the original values from CBNM and NBS. By rounding off the last digit, the weighted mean values were transformed into the jointly certified atom abundance values, given in Table 7.5. The corresponding mass abundances are also given in the same table, together with the overall uncertainty figures. These correspond at least to the 95 % confidence level. They were obtained by enlarging the estimated weighted mean uncertainties for all five abundances to 0.07 percent relative at the discretion of the analysts and in order to assign a same constant uncertainty to all abundances. Thus, allowance is made for eventually existing, still undetected bias effects. This uncertainty range also covers all mean abundance values from CBNM and NBS.

Material	CBNM UF_6MS	CBNM ThIMS	NBS ThIMS	weighted mean *
031	0.320 49 16	0.320 61 47	0.320 76 30	0.320 59
071	0.720 96 17	0.721 19 98	0.720 69 35	0.720 95
194	1.965 75 37	1.967 50 1 73	1.966 40 1 20	1.966 35
295	2.984 32 48	2.987 46 3 90	2.986 90 2 10	2.985 75
446	4.516 68 75	4.520 07 5 19	4.513 80 3 30	4.516 81

* weight factors:
CBNM UF_6MS : 0.50
CBNM ThIMS : 0.25
NBS ThIMS : 0.25

Table 7.4.: $^{235}U/U$ abundances in atom percent and related uncertainties which correspond to a confidence level of 95 %

Material	Atom percent	Mass percent	Uncertainties
031	0.320 6	0.316 6	± 0.000 2
071	0.720 9	0.711 9	± 0.000 5
194	1.966 4	1.942 0	± 0.001 4
295	2.985 7	2.949 2	± 0.002 1
446	4.516 8	4.462 3	± 0.003 2

Table 7.5.: $^{235}U/U$ abundances, jointly certified by CBNM and NBS. The indicated uncertainties, valid for the atom and mass abundances, correspond to a confidence level of 95 %

8. Determination of properties relevant for gamma measurements

In addition to the ^{235}U abundance the following other properties relevant for gamma measurements (4) have been determined:

- chemical composition and impurities
- radiative impurities
- U_3O_8 surface density
- can window thickness.

8.1. Chemical composition and impurities

For the chemical analyses samples were taken at the reception of the material and at the stage of canning (see chapter 4).

The uranium oxide contains water and certain other impurities. In addition it has been indicated by the oxygen-to-uranium ratio measurements performed by the supplier of the material, British Nuclear Fuels, Springfields, UK, that a slight excess of oxygen is present compared to stoichiometric U_3O_8.

The following measurements were carried out:

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

8.1.1. Uranium content

The uranium content (g $U.g^{-1}$ mat.) of the different batches (see Table 8.1.1) was calculated on the basis of weight after calcination of the material at 900°C and subtraction of the estimated sum of the total impurities in the form of oxides (see Table 8.1.2).

The calcination, on 2 to 3 g amounts involved heating in air for 2 hours at 110°C, followed by heating in air for 15 hours at 900°C. From each batch three samples of the material as received and three random samples taken during the filling of the cans were analysed. As no significant differences between the two sets of analyses were observed, an average of the six measurements was made ($n = 6$). On taking into account the uncertainty of the mass determinations and the evaluation of the total impurities, the maximum uncertainty (95 % confidence level) on the element content is estimated to be $\pm$ 1500 $\mu g.g^{-1}$ material as received.

material	g U.g^{-1} U_3O_8
031	0.8456
071	0.8453
194	0.8456
295	0.8452
446	0.8466

Table 8.1.1. Uranium content at the time of canning

8.1.2. Chemical impurities

The total impurity content of the different batches was calculated on the basis of spark source mass spectrometric (SSMS) - and emission spectrographic analyses performed by the CEN-SCK at Mol.

A panoramic analysis, covering 72 elements of each base material was done by Spark Source Mass Spectrometry. Two samplings made during the canning of each material were analysed by emission spectrography. Thirty two elements were rechecked. The results of the analyses prove that no contamination occurred during the preparation step.

The maximum impurity content has been estimated by summing up measured concentrations and the detection limits for a number of elements.

material	Σ imp. $Z \leqslant 30$ μg.g^{-1}	Σ imp. $Z > 30$ μg.g^{-1}
031	< 500	< 6
071	< 300	< 6
194	< 400	< 6
295	< 200	< 6
446	< 1000	< 10

Table 8.1.2. Impurity content

The following elements were measured (or searched for).

$Z \leqslant 30$ Li Be B F Na Mg Al Si P S Cl K Ca Sc Ti V Cr Mn
Fe Co Ni Cu Zn

$Z > 30$ 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 Pr Nd Sm Eu Gd Tb Dy Ho Er
Tm Yb Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Th

8.1.3. Determination of the water content

The moisture content of the material taken at the time of canning was determined by heating the material in an oven at 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 sampling were performed. The uncertainty on these determinations does not exceed $\pm$ 150 $\mu g.g^{-1}$ material.

material	μg $H_2O.g^{-1}$ mat.
031	2525
071	3038
194	2314
295	3000
446	822

Table 8.1.3. Moisture content

8.1.4. Estimation of the light element content

The weight losses observed during calcination consist of water, oxygen and a negligible amount of volatile substances. In 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 ("U_3O_8") results in the figures presented in Table 8.1.4.

material	impurities $Z < 30$ $\mu g.g^{-1}$ mat.
031	$\leqslant$ 4100
071	$\leqslant$ 4600
194	$\leqslant$ 4000
295	$\leqslant$ 5000
446	$\leqslant$ 2500

Table 8.1.4. Maximum content of impurities $Z \leqslant 30$ in U_3O_8

8.1.5. Heavy element content

The content of elements with $Z > 30$ in the different materials does not exceed 10 $\mu g.g^{-1}$ (see Table 8.1.2.).

8.2. Gamma emitting impurities

The occurrence of spurious gamma-lines was tested on one reference sample per abundance by comparing their emission rates to the 185.7 keV line of ^{235}U. The same gamma-counting system applied for testing of the reference samples (Fig. 2-2) was used.

8.2.1. ^{232}U and daughter products

It was essential to determine the ^{232}U impurity content of the materials because gamma lines of ^{232}U daughter products exist in the energy range used by low resolution (NaI) 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 8.2.1 show that the ^{232}U impurities of the materials are small enough to allow the use of the reference samples with NaI counters. Only the peak counting rate ratio of the gamma lines at 238.5 keV and 185.7 keV for the 031 material which was 0.006 in 1982, five years after chemical separation, will grow to a maximum value of about 0.01 in 1987 and introduce a corresponding bias effect.

material	$\frac{\text{counting rate (238.5 keV)}}{\text{counting rate (185.7 keV)}} \cdot 100$ [%] *	$^{232}U/^{235}U \times 10^9$
031	0.62	0.8
071	≤ 0.02 **	< 0.03
194	0.03	0.03
295	0.01	0.01
446	0.08	0.1

* 1982

** Detection level for 238.5 keV gamma-line measurement

Table 8.2.1. ^{232}U content as determined from the gamma peak counting rate of the ^{212}Pb daughter at 238.5 keV relative to ^{235}U at 185.7 keV

8.2.2. ^{233}U, ^{237}U and daughter products

Gamma-lines which might bias low resolution gamma measurements of the ^{235}U abundance, are also known for ^{233}U and for grown-in ^{237}Np because of the short half live of ^{237}U. 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 $^{233}U/^{235}U \leq 5 \cdot 10^{-5}$ and $^{237}Np/^{235}U < 1 \cdot 10^{-6}$. In consequence, bias effects, if any, are smaller than 0.05 %.

8.3. Infinite thickness performance of samples

The infinite thickness performance of the U_3O_8 reference samples is required to ensure that the counting rate from the ^{235}U gamma-radiation at 185.7 keV will correspond to about 99.9 % of the radiation from an infinite thick U_3O_8 layer.

99.9 % gamma response of a U_3O_8 layer is obtained if

$$e^{-\mu_s m_s} = 0.001 \qquad [8.1]$$

where μ_s is the mass attenuation coefficient of U_3O_8 for gamma-radiation with an energy of 185.7 keV and m_s is the surface density of a layer having a minimum value for gamma radiation perpendicular to its surface. For the specification of m_s for the reference samples, m_s = 5.20 g cm^{-2}, a value μ_s= 1.33 g^{-1} cm^2 was used which can be derived from nuclear data tables (21).

The values of both μ_s and m_s were tested experimentally, for the following reasons:

- the literature value of μ_s is specified with an uncertainty of ± 10 % and a taken value for μ_s at the lower limit (μ_s = 1.20 g^{-1} cm^2) would correspond to a gamma response of only 99.8 %;
- the gamma response of the U_3O_8 layer of the reference samples is not only influenced by the mean value of m_s - being specified with an uncertainty of about 0.1 % due to the small tolerances of the can diameter and U_3O_8 sample mass - but also by the variation of m_s over the surface of the sample layer which is introduced by the pressing of the U_3O_8 powder during sample production. This variation may affect the gamma response of the samples and was therefore tested by gamma transmission measurements.

8.3.1. Gamma response of U_3O_8 layers versus surface density

In order to determine the value of μ_s for U_3O_8 and for gamma radiation of 185.7 keV experimentally the gamma counting rate of the 185.7 keV line of ^{235}U was measured for U_3O_8 layers as a function of their surface density, at different viewing angles and was compared with a calculated gamma response for radiation perpendicular to the surface of the layers and suitably chosen values of μ_s.

For the measurements U_3O_8 samples in Al cans have been prepared with U_3O_8 masses ranging from 100 to 220 g, equivalent to surface densities of samples (m_s) ranging from 2.6 to 5.7 g cm^{-2} at a sample diameter of 7.0 cm. The cans were identical to those used for manufacturing the reference samples. Samples were made from material with an abundance $^{235}U/U$ = 0.045. Measurements were performed with the gamma measurement set-up as shown in Fig. 2-2. Different collimator dimensions were chosen, corresponding to height diameter ratios (h/d) of the applied Pb collimator, h/d = 2.0, 1.33 and 0.50 for measuring the variation of the gamma-counting rates relative to the counting rate of a reference sample (m_{so} = 5.2 g cm^{-2}) from material with the same ^{235}U abundance (see Fig. 8.3-1). For the calculation of the corresponding counting rate variations ΔCp/Cp versus m_s - for 185.7 keV gamma radiation only perpendicular to the surface of a sample layer - the formula

$$\frac{\Delta Cp}{C_p} = \frac{(1 - e^{-m_{so}\mu_s}) - (1 - e^{-m_s\mu_s})}{1 - e^{-m_{so}\mu_s}} = \frac{e^{-m_s\mu_s} - e^{-m_{so}\mu_s}}{1 - e^{-m_{so}\mu_s}} \qquad [8.2]$$

has been used for different values of μ_s.

Figure 8.3-1 shows that the measured variations approach the curve ΔCp/Cp calculated for μ_s = 1.27 g^{-1} cm^2 almost correctly when the solid angle decreases (increasing ratio, collimator height h to diameter d) whereas ΔCp/Cp for μ_s = 1.33 g^{-1} cm^2 would only correspond to variations measured for greater solid angles. In consequence it can be assumed that μ_s = 1.27 g^{-1} cm^2 is the approximately correct value for U_3O_8 at 185.7 keV (an uncertainty of about ± 2 % of this value of μs follows from further evaluations). It follows that the 185.7 keV gamma response for the reference samples with m_s = 5.20 g cm^{-2} has a minimum value of 99.86 % of infinite thickness - valid for gamma radiation perpendicular to the can window of the reference samples.

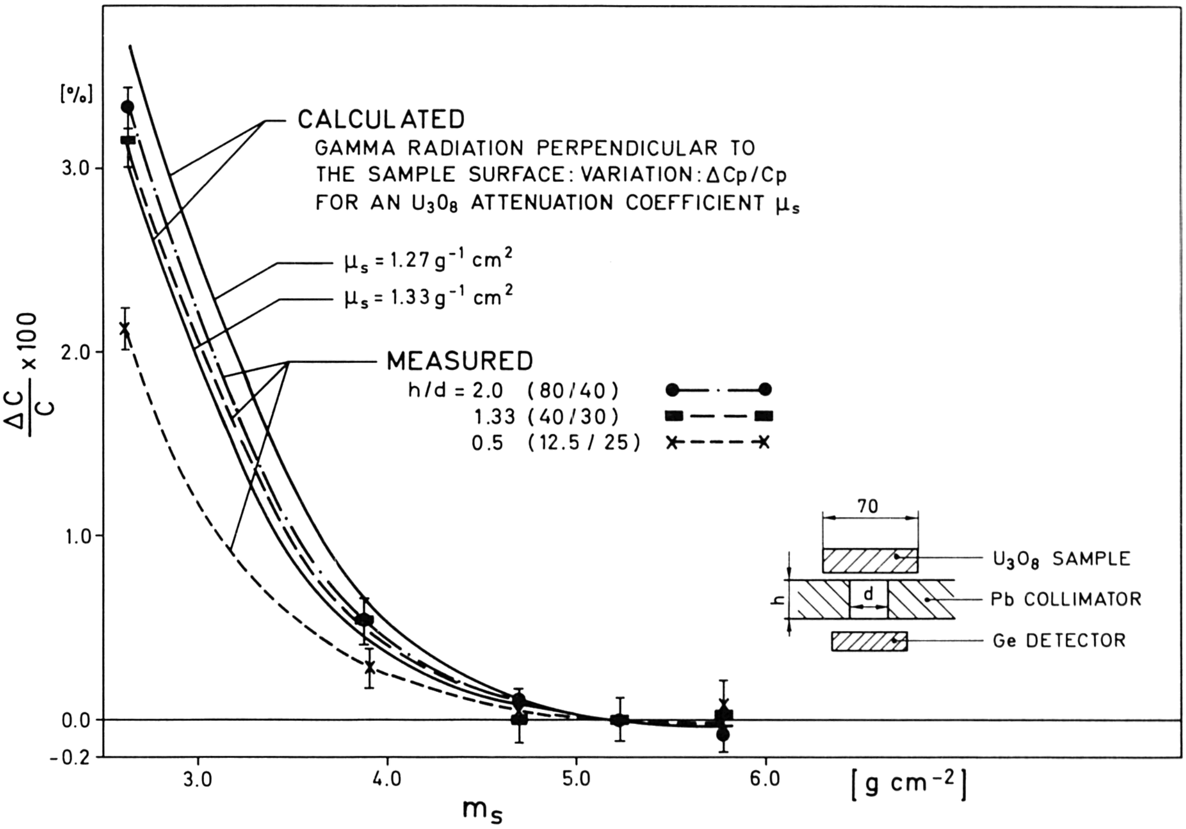


Fig. 8.3-1. Variation of Counting Rate (ΔC/C) of U_3O_8 Samples versus surface density (m_s) relative to a reference sample (m_{so})

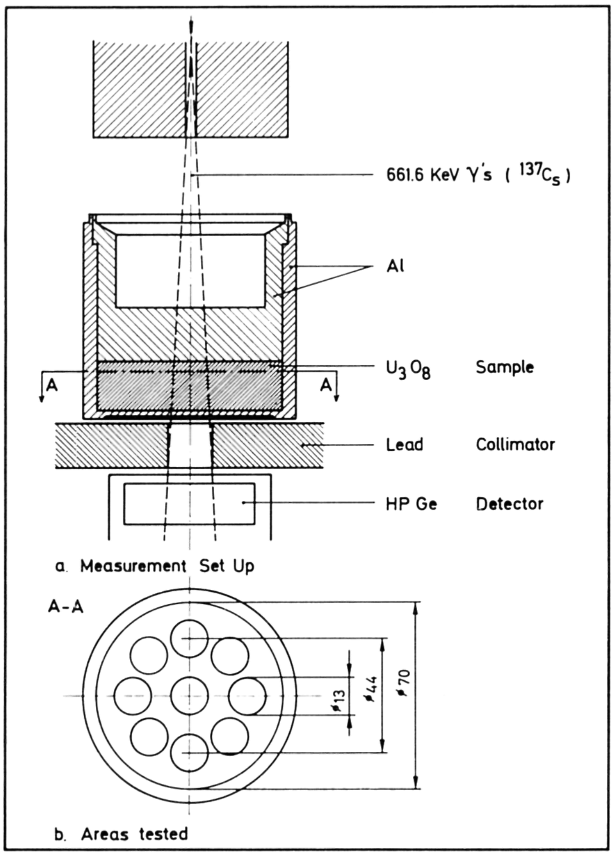
$$\frac{\Delta C}{C} = \frac{C(m_{so}) - C(m_s)}{C(m_{so})} \; ; \quad m_{so} = 5.2 \text{ g cm}^{-2}$$

8.3.2. Uniformity of the U_3O_8 surface density of reference samples

Gamma-transmission measurements on the pressed U_3O_8 powder layers within the Al cans of the reference samples were performed at the centre of the sample surface for all samples and at 9 areas distributed over the sample surface for 8 samples of each of the 5 materials used (see Fig. 8.3-2).

The transmission tests were done with a collimated gamma-beam of ^{137}Cs for the determination of the fluctuations of the counting rate of the transmitted gamma-line at 661.6 keV. They are a measure of the non-uniformity of the U_3O_8 sample mass perpendicular to the sample surface. The measurements were calibrated with well defined U_3O_8 layers. An Al absorber was used as reference for testing the stability of the measured gamma-line counting rate.

Fig. 8.3-2 Set up for U_3O_8 Mass Distribution Uniformity Tests by Gamma-Transmission Measurement



The following results have been obtained for the fluctuations Δm_s of the sample surface density around the mean value of 5.20 g cm^{-2}.

material batch	031	071	194	295	446
fluctuations Δm_s g cm^{-2}	$\leqslant \pm 0.15$				$\leqslant \pm 0.25$

8.3.3. Conclusions

From 8.3.2. above it follows that a value of m_s for the reference samples down to about 5.0 g cm^{-2} is possible. This will change the minimum gamma response of 99.86 % given in 8.3.1 - for radiation perpendicular to the can window of a sample - to a value of about 99.83 %. A maximum gamma response of the reference samples is given for greater solid angles of a measurement system (height to diameter ratio of a chosen collimator, $h/d < 1$ (4)), and may have a value of about 99.97 % equivalent to a mean effective m_s value of about 6.5 g cm^{-2}.

The above circumstances in mind it can be concluded that the gamma response of the reference samples will be in the range of 99.90 ± 0.07 %.

8.4. Can window thickness

The window thickness uniformity of the cans has to fulfil close tolerances as specified in Fig. 8.4-1. Ultrasonic thickness measurements were performed on all the cans using a thickness reference window especially prepared from the Al-alloy ASTM 6061-T6 base material stock used for the manufacturing of all the cans.

Thickness values on this reference window were determined at four well defined measuring places 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 measuring place on the reference window is identical to the surface of each measuring place involved in an ultrasonic determination. The ultrasonic meter has been recalibrated at frequent intervals during the course of a day's operation to minimize errors caused by instrument drift. Under these conditions a maximum uncertainty of ± 5 μm on the window thickness determinations has been achieved.

The cans have been 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 two cans in each set measured, is 0.015 mm (see Fig. 8.4-1).

An example of can window thickness measurements as provided with each reference sample container is given in Fig. 4.1-2.

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

8.5. Evaluation of the uncertainty contributions of a ^{235}U abundance determination by gamma counting

All uncertainty contributions specified in the following sections are maximum values corresponding to a confidence level of about 95 %.

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

2) $s_{13} \leq 0.015 \text{ mm}$
$s_8, s_5, s_4 \leq 0.010 \text{ mm}$

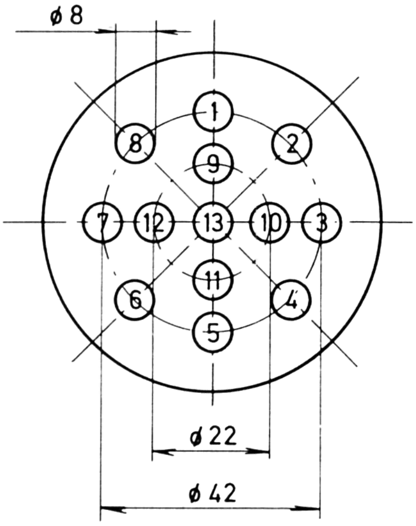
3) For each can $|\bar{x}_8 - \bar{x}_4| \leq 0.005 \text{ mm}$

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

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

and

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



$\bar{x}_{13}$: 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
x_c : thickness control point 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

Fig. 8.4-1.: Specifications for uniformity of window thickness

8.5.1. ^{235}U abundance of reference samples

The stated uncertainties for the ^{235}U isotope abundances of the reference materials are summarized in Table 8.5-1 (see Tables 5.5.2 and 7.5). The values from mass spectrometry measurements, $\Delta A_R/A_R$ (common rounded off values of CBNM and NBS) are contributing directly to the uncertainty of ^{235}U abundance determination by gamma counting, whereas the effect of residual isotopic inhomogeneities $\Delta A_H/A_R$ (or the uncertainty of a verification of the absence of such inhomogeneities) can be smaller, because it is dependent from the material distribution within the reference samples.

Material	031	071	194	295	446
$\pm \Delta A_R/A_R \cdot 100$ [%]	0.07	0.07	0.07	0.07	0.07
$\pm \Delta A_H/A_R \cdot 100$ [%]	0.023	0.013	0.014	0.006	0.012

Table 8.5-1. Uncertainties of ^{235}U abundances

8.5.2. Chemical and physical sample properties

Properties of the reference samples which are influencing 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 $\Delta K/K$ of the correction factors K in formula [2.1].

8.5.2.1. Chemical properties

Measurements on all five material batches and on several samples per batch as described in paragraph 8.1 have shown the maximum impurity content of pure U_3O_8 to be as follows:

$Z \leqslant 30$: $\leqslant 5000\ \mu g\ g^{-1}$

$Z > 30$: $\leqslant 10\ \mu g\ g^{-1}$

This corresponds to a gamma attenuation equivalent to an uncertainty of:

$$\frac{\Delta K_m}{K_m} \cdot 100 \leqslant 0.051\ \%.$$

The major effect on the above figure is coming from the water content of the materials ($\leq 3200\ \mu g\ g^{-1}\ U_3O_8$).

8.5.2.2. Physical sample properties

The U_3O_8 surface density and can window thickness of all reference samples were tested.

- U_3O_8 surface density

  The measured residual inhomogeneity of the U_3O_8 surface density over the sample surface, perpendicular to the can window, of $< \pm 5\ \%$ for a mean surface density of $5.2\ g\ cm^{-2}$ is part of an overall uncertainty of:

  $$\frac{\Delta K_s}{K_s} \cdot 100 < \pm 0.07\ \%.$$

- Aluminium can window thickness

  An uncertainty of the effective can window thickness of $< \pm 0.02$ mm between reference samples from different sets will introduce an uncertainty of the measured counting rate of:

  $$\frac{\Delta K_c}{K_c} \cdot 100 < \pm 0.10\ \%.$$

  In both cases the uncertainties are given for viewing angles encountered in typical detector/collimator configurations corresponding to collimator height to diameter ratios h/d down to about 0.3 (see also ref. 4)

8.5.3. Overall gamma counting uncertainty of reference samples

The gamma-counting uncertainty contributions from the reference sample properties, outlined in the previous paragraphs are maximum values. They are independent in origin and can be used therefore for a calculation of the maximum overall gamma emission rate non-uniformity at 185.7 keV of a series of reference samples from one material batch as follows:

$$\frac{\Delta C}{C}\ \text{(calculated)} \leq \sqrt{\left(\frac{\Delta A_H}{A_R}\right)^2 + \Sigma_K \left(\frac{\Delta K}{K}\right)^2}$$

With: $\frac{\Delta A_H}{A_R} < \pm\ 0.023\ \%$

and the quadratic summation of the maximum uncertainties for the correction factor K,

$$\Sigma\left(\frac{\Delta K}{K}\right)^2 = \left(\frac{\Delta K_m}{K_m}\right)^2 + \left(\frac{\Delta K_s}{K_s}\right)^2 + \left(\frac{\Delta K_c}{K_c}\right)^2 \qquad \text{(see formula [2.1])},$$

using the values: $\Delta K_m/K_m < 0.051\ \%$; $\Delta K_s/K_s < 0.07\ \%$, and $\Delta K_c/K_c < 0.10\ \%$ it follows for the maximum overall gamma counting uncertainty of samples with the same ^{235}U abundance:

$$\frac{\Delta C}{C} \cdot 100 \text{ (calculated)} < \pm\sqrt{0.023^2 + 0.051^2 + 0.07^2 + 0.10^2}\ \%$$

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

This value is practically not affected by $\frac{\Delta A_H}{A_R}$ (influence smaller than 0.002 %) and in some agreement with test results outlined in the following sections, 8.6 and 9.3.

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

$$\frac{\Delta C}{C} \text{ (overall)} = \sqrt{\left(\frac{\Delta A_R}{A_R}\right)^2 + \left(\frac{\Delta C}{C}\right)^2 \text{ (calculated)}}$$

With the value of $\Delta A_R/A_R = \pm\ 0.07\ \%$ in Table 8.5-1 it follows:

$$\frac{\Delta C}{C} \cdot 100 \text{ (overall)} < \pm\sqrt{0.07^2 + 0.023^2 + 0.051^2 + 0.07^2 + 0.10^2}\ \%$$

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

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 $\Delta K_c/K_c < 0.07$ instead of < 0.10).

8.6 Overall uniformity of reference samples

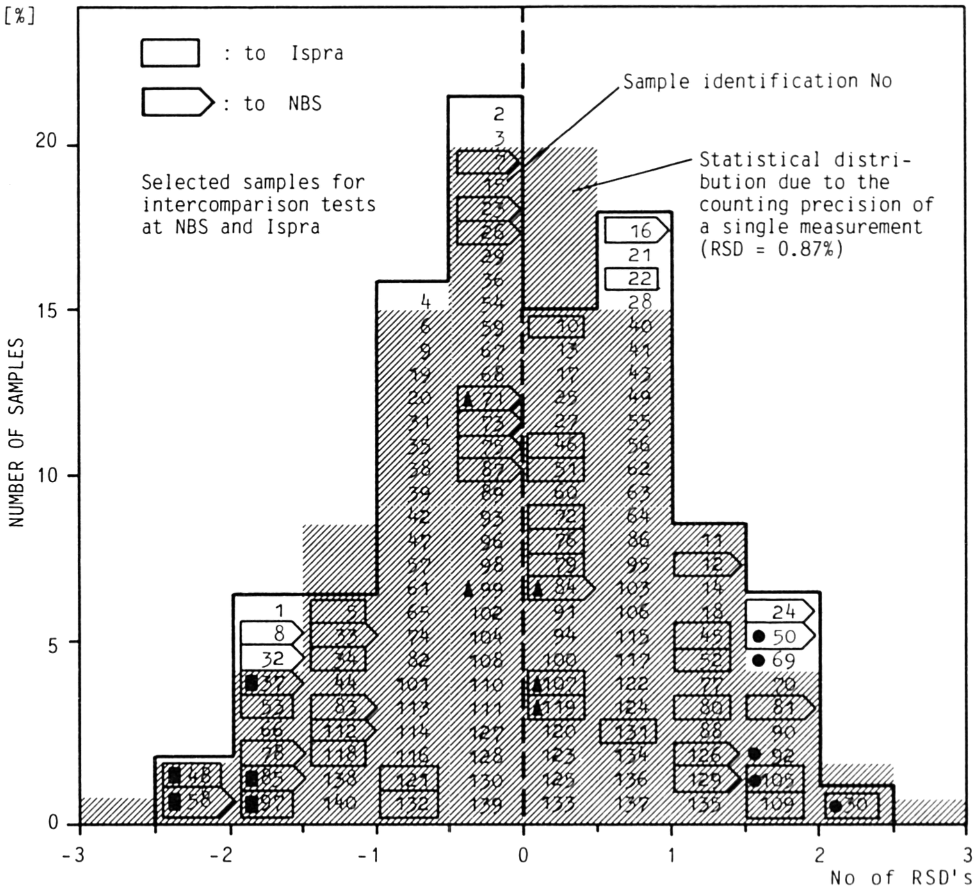
Different series of gamma measurements have been performed for testing with a high resolution gamma spectrometer system (see Fig. 2-2) the uniformity of the reference samples with respect to the gamma-counting rate of ^{235}U at 185.7 keV as a measure of the overall uniformity of sample properties affecting the uncertainty of ^{235}U abundance measurements. For all tests the precision values given are one RSD (relative standard deviation) and the energy resolution of the applied spectrometer [FWHM] was 0.83 keV at 185.7 keV.

a) Measurement of all samples at the center area of the can window

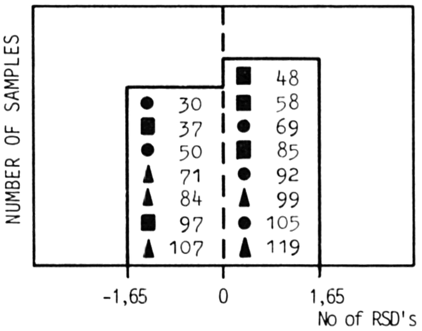
In performing fabrication tests for all 140 samples of each of the five materials the 185.7 keV gamma counting rate has been measured with a low precision (1 RSD) between ± 0.5 % and ± 0.9 % and using a Pb collimator with a diameter of 25 mm and a height of 40 mm (low precision tests, see Figs. 8.6-1.1a to 8.6-1.5a). The tests were done relative to a calibration sample (^{235}U abundance of 2.98 atom %) in order to minimize the effect of detector efficiency shifts and were also corrected for differences in can window thickness.
The agreement of the measured counting rate distributions of samples around average values with the statistical distributions due to the counting precisions of single measurements (shaded areas for the assumed distribution of repeated measurements on a single sample) was tested by chi square tests for the goodness of fits (31,32). Probability values between 0.65 and 0.90 were calculated, confirming the probable statistical nature of the measured distributions and in such a way the uniformity of samples for each material type.
For an additional confirmation of sample uniformities two kinds of samples were selected from the low precision tests for high precision measurements:

- samples with counting rates approximately equal to the mean counting rates;
- samples with counting rates very different from the mean counting rates.

The selected samples were sent to JRC Ispra and NBS Washington for verification measurements (24 each per material type to JRC Ispra and NBS Washington, see section 9.3) and some were used partly for own high precision measurements (15 samples as identified in Figs. 8.6-1 with black rectangles, triangles and circles).

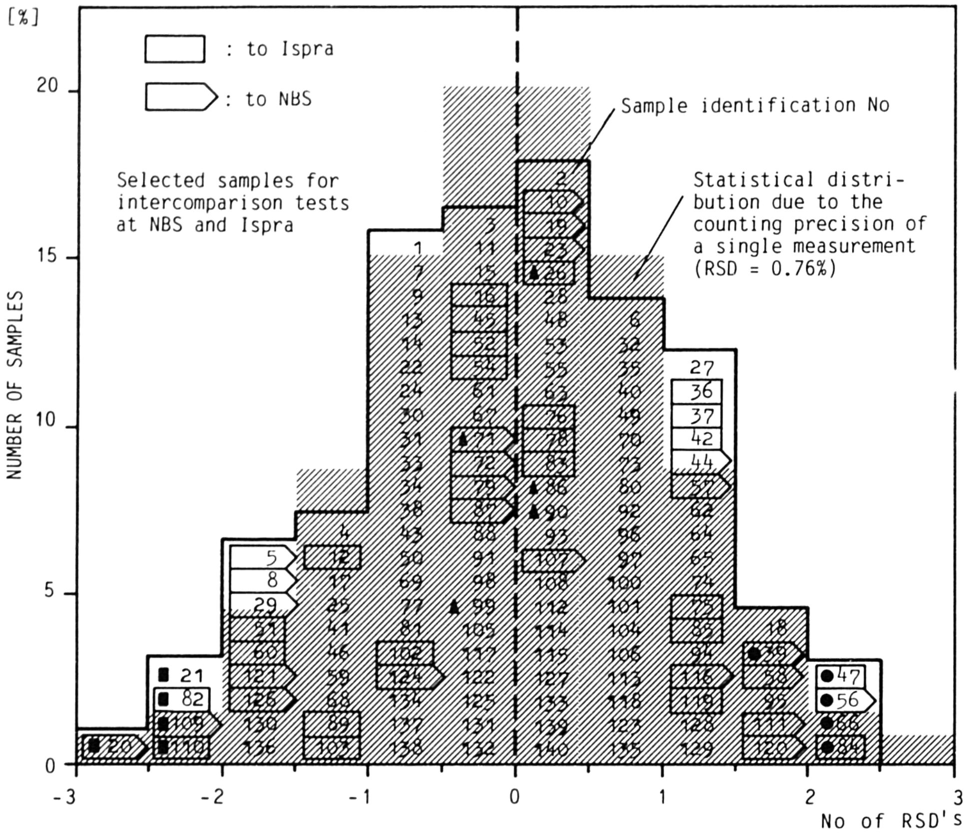


a. Low precision test of samples (RSD = 0.87%)

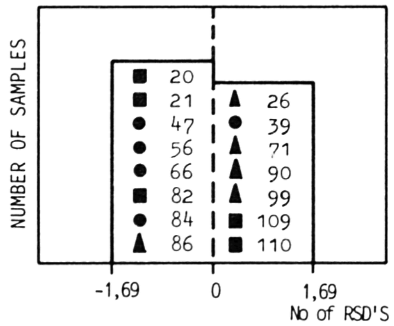


b. High precision test of samples (RSD = 0.28%) as identified above

Fig. 8.6-1.1. Gamma counting rate uniformity of U_3O_8 reference samples at 185.7 keV (corrected for differences in can window thickness); Material : 031

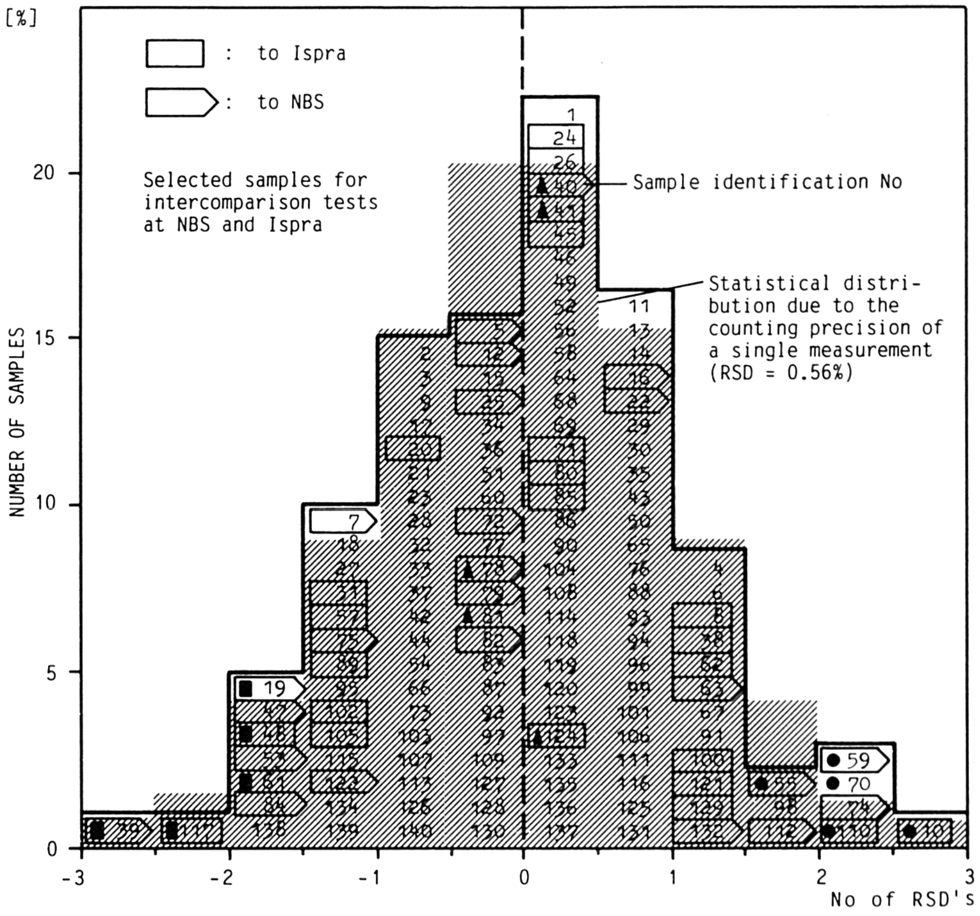


a. Low precision test of samples (RSD = 0.76%)

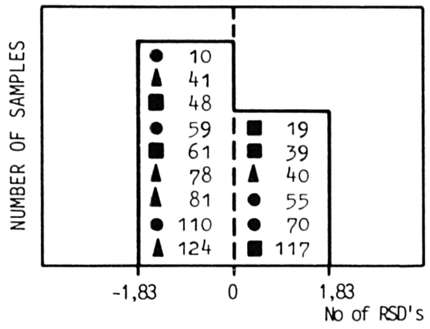


b. High precision test of samples (RSD = 0.29%) as identified above

Fig. 8.6-1.2. Gamma counting rate uniformity of U_3O_8 reference samples at 185.7 keV (corrected for differences in can window thickness); Material : 071

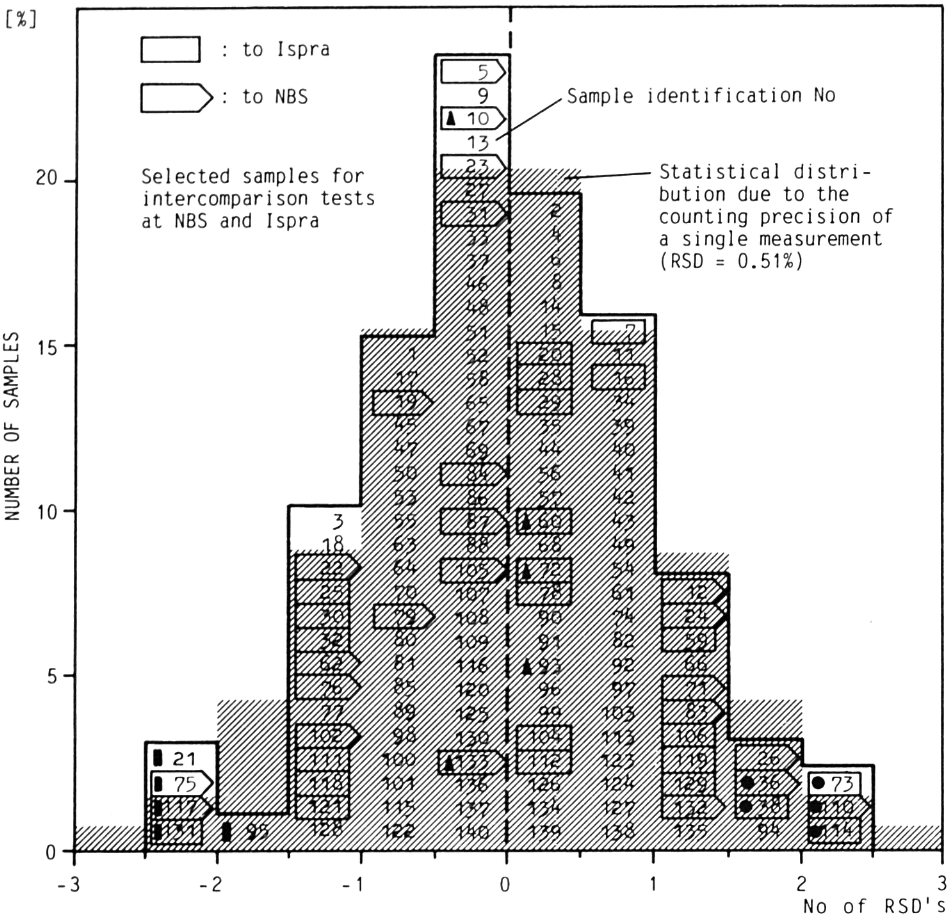


a. Low precision test of samples (RSD = 0.56%)

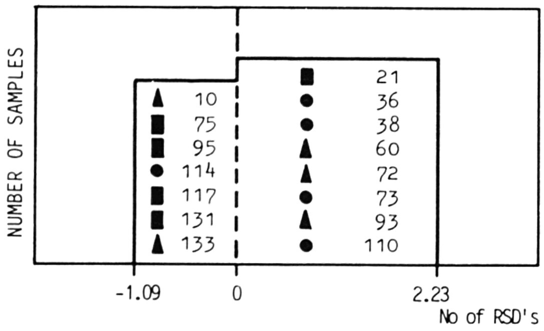


b. High precision test of samples (RSD = 0.19%) as identified above

Fig. 8.6-1.3. Gamma counting rate uniformity of U_3O_8 reference samples at 185.7 keV (corrected for differences in can window thickness); Material : 194

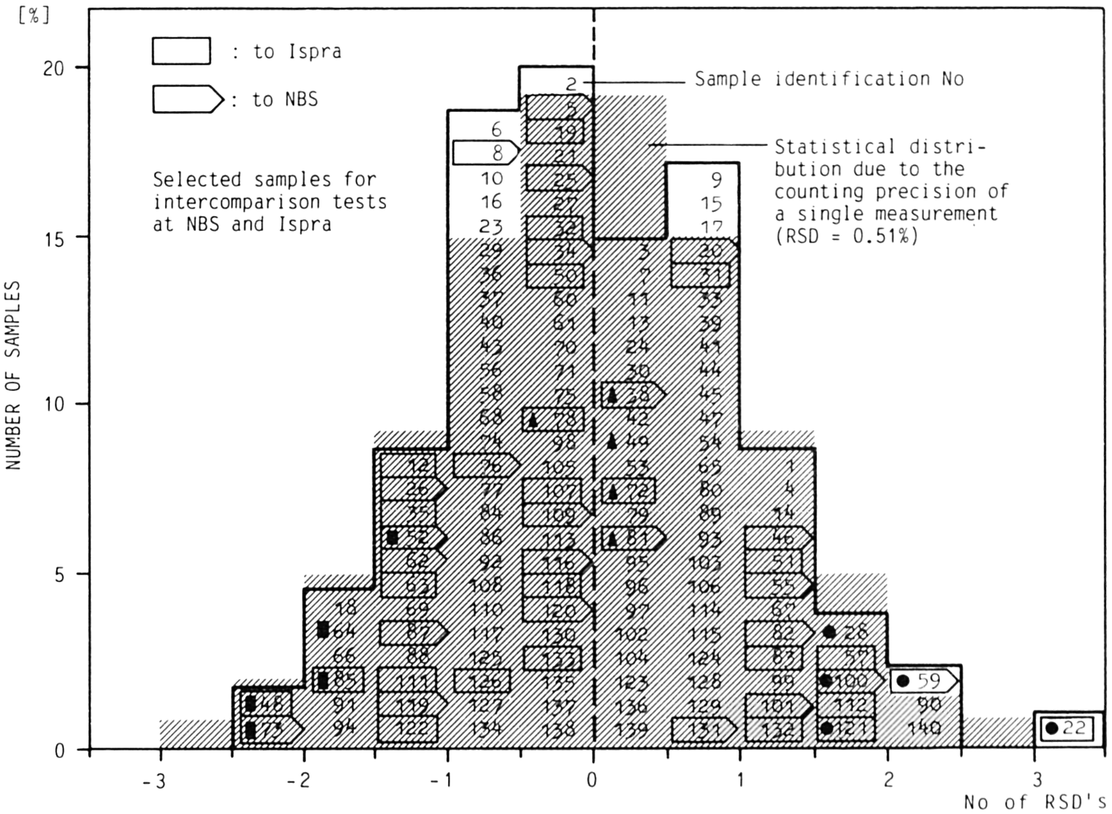


a. Low precision test of samples (RSD = 0.51%)

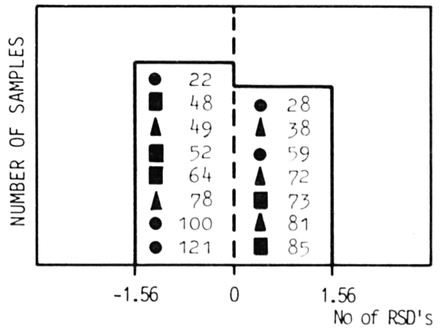


b. High precision test of samples (RSD = 0.21%) as identified above

Fig. 8.6-1.4. Gamma counting rate uniformity of U_3O_8 reference samples at 185.7 keV (corrected for differences in can window thickness); Material : 295



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



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

Fig. 8.6-1.5. Gamma counting rate uniformity of U_3O_8 reference samples at 185.7 keV (corrected for differences in can window thickness); Material : 446

b) Measurement of 15 selected samples with high precision

The 15 samples of each material type which were selected from the center and tail areas of the counting rate distributions as described before have been measured under the same measurement conditions as given under a) but with counting precisions (RSD) between ± 0.16 % and ± 0.29 % (high precision tests, see Figs. 8.6-1.1b to 8.6-1.5b).
The distribution widths of results around average values are smaller than ± 2 RSD and confirm the validity of the statistical nature of the distributions in spite of the higher measurement precisions compared to case a) (see also that results from specific samples appearing in the lower tail area of the "low precision" distributions are reappearing in the upper part of the "high precision" distributions and vice versa). The reference ("average") counting rate ratio of the "high precision" tests has been taken from the "low precision" tests. For this reason the results in Fig. 8.6-1.4b are not symmetrical to the reference value.

c) High precision measurements of all material 446 samples

The counting rates of all 140 samples from the material 446 relative to the counting rate of a calibration sample (one sample from the same series) have been redetermined with the same measurement conditions as described under a), b) but with a Pb collimator of 30 mm diameter and 40 mm height and with a counting precision (1 RSD) of ± 0.14 % (see Fig. 8.6-2). The tests were done relative to an arbitrarily chosen sample out of the measured series and the results were corrected for differences in sample window thickness. The distribution of measurement results was compared as under a) to the statistical distribution from the counting precision of a single measurement (shaded area, for the expected distributions from repeated measurements on one sample) by a chi square test for the goodness of fit. The obtained probability value of about 0.8 confirmed also for this high precision test the probable statistical nature of the distribution of measurement results. One reason for the measurement of all material 446 samples with high precision was to verify the uniformity of sets of reference samples (see also set-specific measurements as described under d) below).

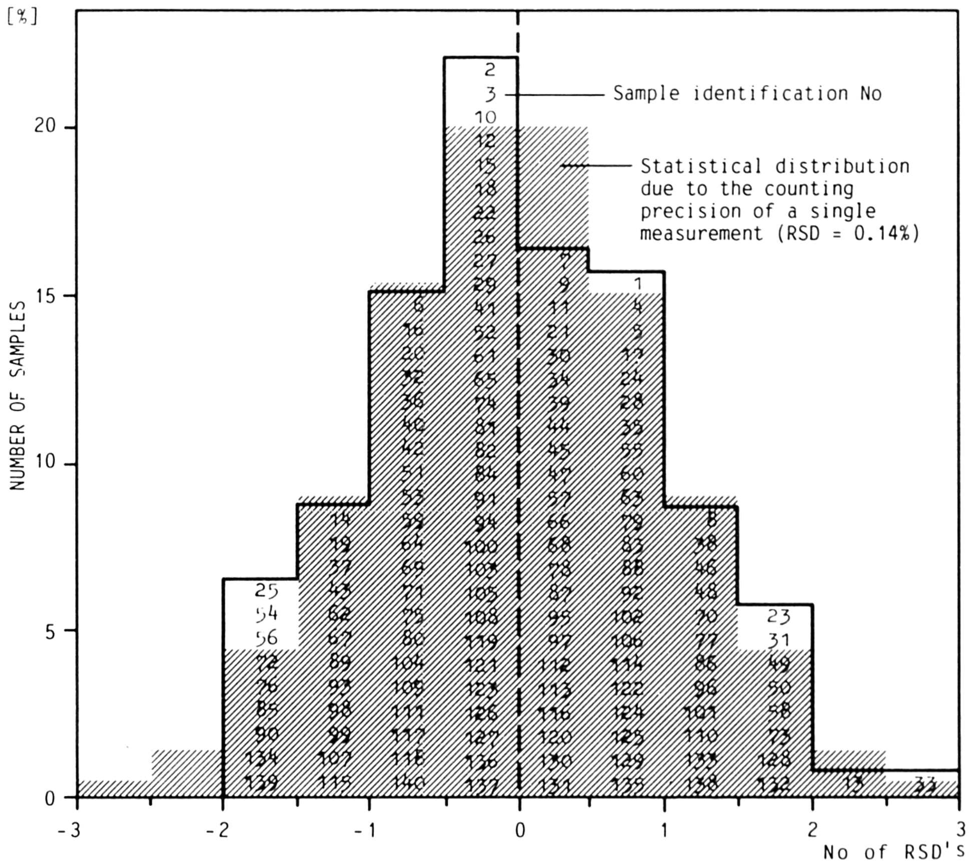


Fig. 8.6-2. High precision test of the gamma counting rate uniformity of U_3O_8 reference samples at 185.7 keV (corrected for differences in can window thickness); Material : 446

As a conclusion from the tests under a), b) and c), all concerned with the sample uniformity tests summarized in Figs. 8.6-1 and 8.6-2, it can be stated that a non-uniformity of samples was not measurable and will be determined mainly by the can window non-uniformity of samples ($\Delta K_c/K_c$, not exceeding 0.1 %). These results were confirmed by further high precision tests at JRC Ispra and NBS Washington (see 9.3).

d) Set-specific high precision counting rate tests

High precision tests of the gamma counting rate at 185.7 keV (with the same measurement conditions as under c)) have been performed also for each individual set of the existing 50 CBNM sets provided with ultrasonic seals in order to make available set-specific test results for future owners. In order to reduce measurement times for a set of samples these were measured with a counting precision (1 RSD) being in some proportion to the ^{235}U abundance (A_ν) of the sample materials (1 RSD [%] $\leq \pm$ 0.5 x (0.25 + 0.1/A_ν) with A_ν in at.%).
The test results are presented in form of a fluctuation of measured gamma counting rates of samples (ΔC_n) around an average value vs. A_ν. The counting rates $C(A_\nu)$ have been normalized for that purpose to the corresponding A_ν values:

$$C_n(A_\nu) = \frac{C(A_\nu)\ K_\gamma}{A_\nu[\text{at.\%}]}\ , \qquad \frac{\Delta C_n}{C_n}\ [\%] = \frac{C_n(A_\nu) - \overline{C_n(A_\nu)}}{\overline{C_n(A_\nu)}} \times 100$$

where $\overline{C_n(A_\nu)}$ is the weighted average value of all measurements on a set and K_γ is a correction for small bias effects from two gamma lines near 185.7 keV (from ^{234m}Pa and ^{234}Pa as daughter products of ^{238}U).

Figure 8.6-3. gives the average values of $\Delta C_n/C_n$ for measurements on the 50 samples per material. They show the linearity of the calibration curve for the applied instrumentation system as well as the agreement between ratios of ^{235}U abundance values obtained from material characterization by mass spectrometry and the corresponding ratios of measured gamma counting rates.

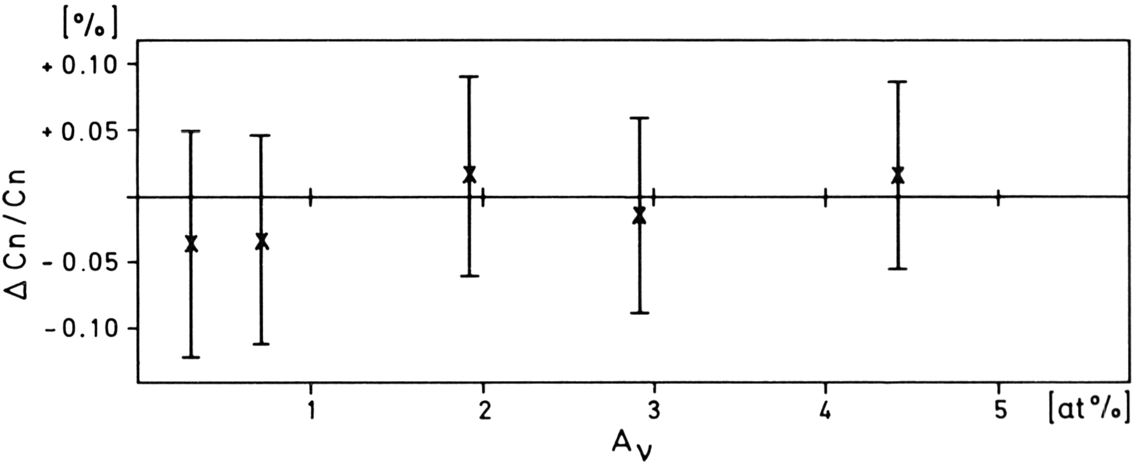


Fig. 8.6-3. Average variation of normalized gamma counting rates at 185.7 keV versus ^{235}U abundance A_ν for 50 sets of samples; uncertainties are 2s, they include the mass spectrometry uncertainties of A_ν values

9. Verification measurements

Verification of measurements leading to certified quantities can be considered as part of the certification procedure. It should be done by laboratories, independent from those issuing the certificate, and having some competence in the analytical field concerned. In general, much less effort is spent on verification work (in comparison with the efforts made to establish the certified values) and, therefore, the obtained uncertainties are larger. With this prospect the ^{235}U/U abundances were measured by the Energieonderzoek Centrum Nederland (ECN), Petten, NL, and the New Brunswick Laboratory (NBL), Argonne, Illinois, USA.

Additional measurements on the uranium content of the U_3O_8 material were performed by NBL and ECN as well.

The uniformity of the U_3O_8 layers in the reference samples were tested by gamma spectrometric measurements at NBS and JRC, Ispra. Although not strictly falling under the term "verification" as defined above, the results are presented in this chapter in order to demonstrate the overall compatibility of the results.

9.1. ^{235}U/U Abundance

In the case of the EC NRM 171/NBS SRM 969 the certified quantities are the ^{235}U/U abundances. The only sufficiently accurate method for their determination is mass spectrometry, calibrated by synthetic isotope mixtures. CBNM and NBS results are fully based on own mixtures (NBS directly or via the NBS-SRM's). Therefore, two completely independent routes were followed and the good agreement obtained represents a real mutual verification.

The measurement results from ECN and NBL are given in Table 9.1.1., compared to the certified values. The results from ECN and NBL are presented as they were transmitted, i.e. in mass or atom percent, and with 1s or 2s measurement precision. For mass spectrometric calibration NBS SRM 500 was used in both cases.

Material	^{235}U/U certified mass abundances (+ 2s uncert.)	^{235}U/U mass abundances ECN (+1s uncert.)*	^{235}U/U certified atom abundances (+ 2s uncert.)	^{235}U/U atom abundances NBL (+2s uncert.)*
031	0.003 166	0.003 174	0.003 206	0.003 203
	2	5	2	7
071	0.007 119	0.007 116	0.007 209	0.007 207
	5	5	5	7
194	0.019 420	0.019 421	0.019 664	0.019 657
	14	13	14	15
295	0.029 492	0.029 497	0.029 857	0.029 843
	21	13	21	39
446	0.044 623	0.044 646	0.045 168	0.045 162
	32	15	32	39

* Precision of the measurements only

Table 9.1.1.: Comparison of ^{235}U/U abundances from other laboratories

9.2. Uranium content

Uranium contents were determined by NBL and ECN respectively, and NBL also measured the total weight loss on heating at 110°C. The results are given in Tables 9.2.1. and 9.2.2..

Material	NBL			ECN		
	g U·g^{-1} U_3O_8*	1s uncertainty	n	g U·g^{-1} U_3O_8*	1s uncertainty	n
031	0.847 685	± 0.000 027	5	0.845 445	± 0.001 2	6
071	0.847 688	± 0.000 054	5	0.846 414	± 0.000 7	6
194	0.847 800	± 0.000 083	5	0.847 640	± 0.000 6	6
295	0.847 758	± 0.000 112	5	0.848 118	± 0.000 4	6
446	0.847 488	± 0.000 020	5	0.847 623	± 0.000 4	6
NBS-SRM	0.847 783	± 0.000 072	15			
950**	0.847 737	± 0.000 038	8			
EC-NRM 110***				0.881 13	± 0.000 22	10

* Dried at 110°C, ignited at 800°C, corrected for isotopic composition

** Certified values = 99.968 ± 0.020 % U_3O_8 (0.847 731 g U·g^{-1})

*** Certified value 0.881 34 ± 0.000 13 g U·g^{-1}

Table 9.2.1.: Uranium content determination by NBL and ECN

Material	$\mu g \cdot g^{-1}$ U_3O_8
031	1800
071	2300
194	1800
295	2200
446	600

Table 9.2.2.: Total mass loss at 110°C determinations by NBL

The aim of the uranium analyses was to verify the correctness of the statement that the "U_3O_8" consists of stoichiometric U_3O_8 with a maximum of 0.5 % impurities. Pure stoichiometric U_3O_8 (of the given isotopic abundances) contains between 0.8479 and 0.8480 g $U \cdot g^{-1}$. Oxide containing 0.005 $g \cdot g^{-1}$ impurities should only have about 0.8438 g $U \cdot g^{-1}$. All direct uranium analyses (Table 9.2.1) gave higher results than this which confirms the statement that the total impurities are less than 0.5 % maximum.

For the transformation of the NBL uranium content values into figures valid for the U_3O_8 at the time of canning, the results of the total mass losses at 110°C (Table 9.2.2) were taken into account These values are given in Table 9.2.3 together with those from CBNM (see Table 8.1.1).

Material	NBL	CBNM
	μg $U \cdot g^{-1}$ U_3O_8	
031	0.8462	0.8456
071	0.8458	0.8453
194	0.8463	0.8456
295	0.8549	0.8452
446	0.8469	0.8466

Table 9.2.3.: Uranium content at the time of canning

Procedures used at NBL were as follows:

Sample Ignitions and Aliquant Preparation

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

The samples were then dried at 110°C for two hours, cooled and weighed. A weighing procedure similar to the above was necessary because successive weighings gave increasing masses. The samples were placed in a furnace at 800°C for two hours, cooled and weighed, again plotting each set of weighings. The samples were reignited at 800°C for an additional hour, cooled and reweighed.

In order to assure 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 additional aliquants from each sample were placed in beakers for isotopic analysis.

Chemical Assay

Chemical assay aliquants were dissolved in phosphoric acid and titrated according to the NBL High Precision Method (30) following the previously agreed upon Characterization Plan. NBS 950b (U_3O_8) was ignited at 800°C for one hour and assayed for a control standard.

Procedures used at ECN were as follows:

From each batch 6 samples were dissolved in nitric acid. The applied method was the NBL modified Davies and Gray titration for small amounts of uranium.

9.3. Gamma-counting uniformity tests at JRC Ispra and NBS

Uniformity tests by high precision gamma counting have been performed at JRC Ispra and at NBS on 48 reference samples (24 each) from each of all five materials. For the selection of samples criteria as given under 8.6a and on Figures 8.6-1.1 to 8.6-1.5 were applied.

Measurements were performed with a counting precision of ± 0.052 % to ± 0.26 % (see Figs. 9.3-1 and 9.3-2).

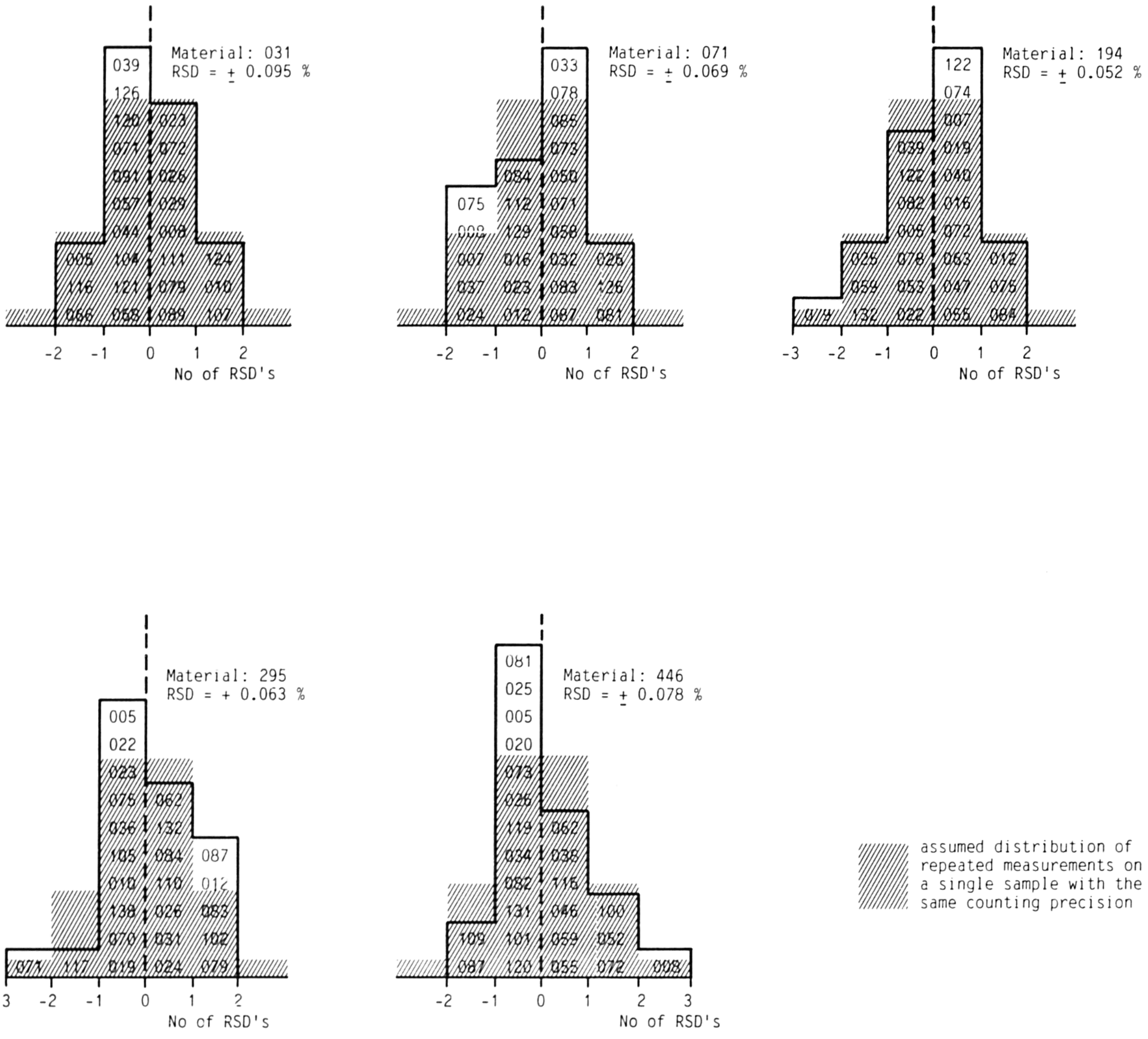


Fig. 9.3-1. Testing the gamma counting rate uniformity of the ^{235}U gamma line at 185.7 keV by NBS, Gaithersburg on 24 U_3O_8 reference samples of each material (corrected for differences in can window thickness)

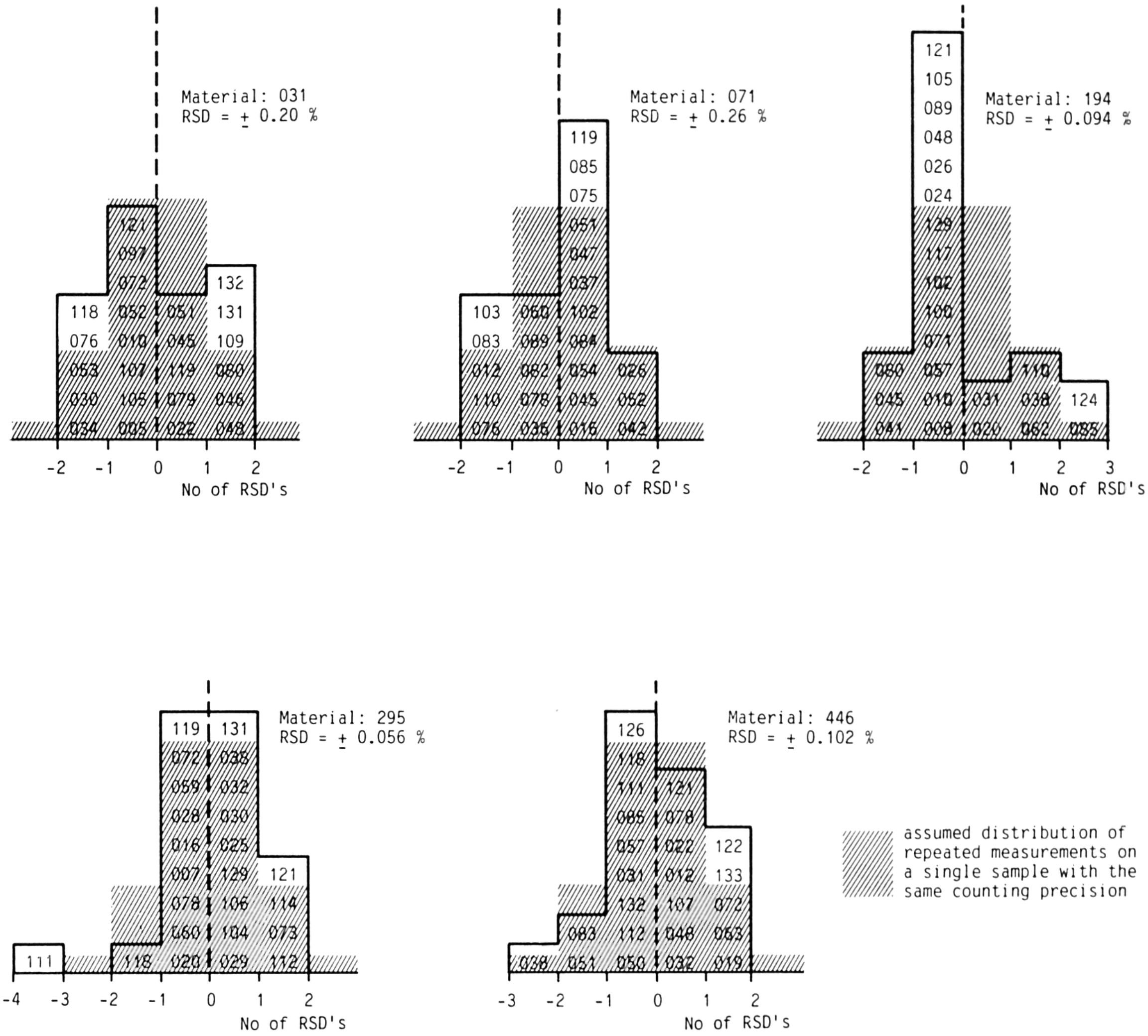


Fig. 9.3-2. Testing the gamma counting rate uniformity of the ^{235}U gamma line at 185.7 keV by JRC-Ispra on 24 U_3O_8 reference samples of each material (corrected for differences in can window thickness)

As a comparison of the distributions of measured counting rates with the statistical distributions from the counting precision of a single measurement (shaded areas for the expected distributions of repeated measurements on one sample) chi square tests for the goodness of fits were performed. As a result probability values between 0.95 and 0.47 were obtained (exception: p = 0.06 for Ispra measurements on 194 material samples) which confirmed that the measured distributions are to a large extent in accordance with counting statistics and in such a way the uniformity of the measured samples.

Performance of gamma counting tests at NBS (22)

A high resolution gamma spectrometer system was used by NBS for testing the uniformity of the ^{235}U characteristic gamma counting rate of 24 reference samples of each of the five materials. The resolution [FWHM] was about 1.0 keV at 185.7 keV.

For counting rate determination, peak integration over the two adjacent gamma lines of ^{235}U at 185.7 keV and 182.7 keV, using channel by channel summation over the energy region 180.8 to 190.0 keV has given most reproducible results (with background integration over energy regions adjacent to the peak energy region, from 178.5 to 180.8 keV and 190.0 to 192.5 keV).

A special collimator assembly was fabricated from lead (collimator opening: 50 mm ø and 15 mm height) in order to ensure maximum stability of the counting geometry of the spectrometer system and reproduceable can positioning of samples. The assembly was fixed to the germanium detector system as shown in Fig. 9.3-3.

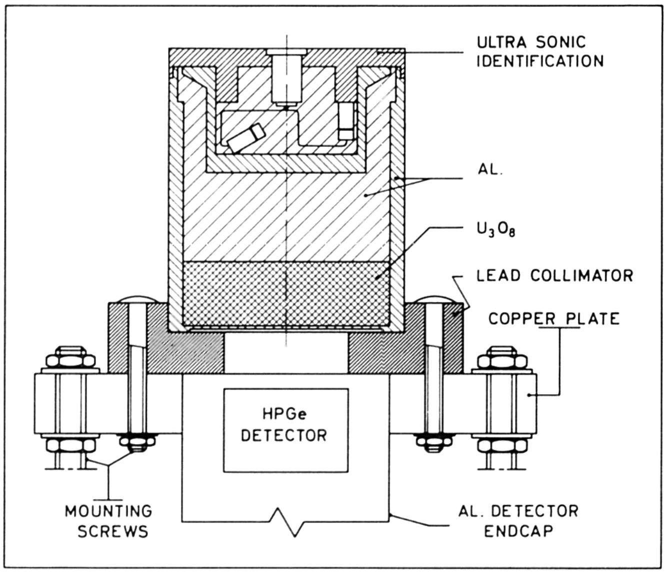


Fig. 9.3-3. NBS gamma counting assembly

The reference sample tests were compared with measurements on a calibration sample, provided by CBNM and almost identical in lay-out with the reference samples (^{235}U abundance of 2.98 at.%). The measurement results were corrected for residual differences in can window thickness between the calibration sample and the tested reference samples.

9.4. Conclusion

The results of the verification measurements support the results of the measurements which led to the values given on the draft certificate (Annex A).

10. List of Working Group members

From national laboratories in Europe:

R.J.S. Harry (Chairman)	Stichting Energieonderzoek Centrum Nederland, Petten, Nederland
J. Legrand[*]	Commissariat à l'Energie Atomique, CEA, Centre d'Etudes Nucléaires, CEN Saclay, France
H. Ottmar	Kernforschungszentrum Karlsruhe, KfK, Bundesrepublik Deutschland
F.J.G. Rogers[**]	United Kingdom Atomic Energy Authorities, UKAEA, Atomic Energy Research Establishment Harwell, United Kingdom

From USA:

B.S. Carpenter	National Bureau of Standards, Gaithersburg, MD, USA

From the Commission of the European Communities:

P. De Bièvre	Joint Research Centre, Central Bureau for Nuclear Measurements, CBNM, Geel, Belgium
H.L. Eschbach	
R. Lesser	
H. Meyer	
W. Nagel / F. Quik (Secr.)	
J. Van Audenhove	
M. Cuypers	Joint Research Centre, Ispra Establishment, Ispra, Italy

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[*] represented in one meeting by:

B. Chauvenet	Commissariat à l'Energie Atomique, CEA, Centre d'Etudes Nucléaires, CEN Saclay, France

[**] represented in one meeting by:

J. Dunbar	British Nuclear Fuels plc, Springfields, United Kingdom

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APPENDIX A

Certified Nuclear Reference Material

Certificate of Analysis

EC CERTIFIED NUCLEAR REFERENCE MATERIAL 171
^{235}U Isotope Abundance Certified Reference Material (U_3O_8)
for Gamma-Spectrometry.

^{235}U/U Abundances

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

The indicated uncertainties, valid for the atom and mass abundances, correspond to a confidence level of 95%.
This certificate applies to the reference samples:

CBNM 031 -
CBNM 071 -
CBNM 194 -
CBNM 295 -
CBNM 446 -

The Certified Nuclear Reference Material has been prepared in cooperation with the National Bureau of Standards (NBS), Gaithersburg, MD, USA. EC Certified Nuclear Reference Material 171 corresponds to NBS Standard Reference Material 969

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Purpose

This certified Nuclear Reference Material (NRM) is intended to be used for the non-destructive determination of the abundance of ^{235}U in homogeneous uranium bulk materials by gamma spectrometry, using its characteristic radiation at 185.7 keV. For this purpose four parameters are specified in addition to the certified $^{235}U/U$ abundances: can window thickness, chemical purity of the U_3O_8, thickness of the U_3O_8 layer, and gamma-emitting impurities.

Description

EC NRM 171 (European Community Certified Nuclear Reference Material No. 171), as well as its equivalent NBS SRM 969 (National Bureau of Standards Standard Reference Material No. 969), consists of a set of five sealed cans, each of which is defined as a reference sample. Each reference sample contains 200 g U_3O_8 with one of five different $^{235}U/U$ isotope abundances, the nominal mass percents of which are 0.31; 0.71; 1.94; 2.95 and 4.46. In addition, an empty can is provided for measurements on material of unknown $^{235}U/U$ abundance under similar geometrical conditions.

The can material consists of aluminium alloy type ASTM-6061-T6.

The outer can diameter is 80 mm, the can height is 90 mm. The bottom with specified thickness serves as window for the emitted gamma radiation.

Identification

Each reference sample has the following marks engraved on the outer can surface:

- CBNM or NBS, i.e. the name of the body issuing the certificate;
- a three-digit number relating to the nominal $^{235}U/U$ mass abundance, e.g. the number 031 refers to a nominal abundance of 0.31 percent;
- a three-digit number specific for each NRM, i.e. for each set of reference samples.

This certificate relates to the set of reference samples with the numbers indicated on the first page.

Characterization

The uranium isotope abundances were determined by thermal ionization mass spectrometry at CBNM and NBS, and by UF_6 mass spectrometry at CBNM.

At CBNM all measurements were calibrated by synthetic uranium isotope mixtures, prepared from purified ^{235}U and ^{238}U isotopes.

At NBS the nominal 0.71 percent abundance material was calibrated by synthetic isotope mixtures, the others were calibrated relative to NBS-SRM U-500.

The detailed certification report for EC NRM 171 was prepared by CBNM and published as Report COM 4153. During its finalization CBNM was assisted by a Working Group of European experts and a NBS representative.The corresponding USA certification report is numbered NBS-260-96.

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 spectrometric characterization, and the control of the $^{235}U/U$ homogeneity. The resulting figures were enlarged to 0.07% for all five abundances. The attributed confidence level is 95%.

All other properties of an individual reference sample, relevant for accurate abundance measurements by gamma spectrometry at the 185.7 keV line with a high resolution germanium detector, are at uncertainty levels which keep their total impact on an abundance measurement within ± 0.14%. Thickness uniformity of the reference sample window, chemical purity of the U_3O_8, and the effective U_3O_8 surface density were taken into account.

By combining all uncertainties including that for the $^{235}U/U$ abundance according to the principles applicable to independent error contributions, this results in a maximum overall uncertainty of ± 0.16% for this nuclear reference material when used for gamma spectrometric calibrations.

Notice to the Users

Corrections have to be made, if the degree of "infinite thickness" for the gamma radiation at 185.7 keV of an unknown sample deviates from the corresponding mean value of 99.90% of the reference samples.

A special Users Manual (Report KfK 3752 (1984)) has been prepared to facilitate the correct use of EC NRM 171. The manual describes in detail the principles of the $^{235}U/U$ abundance measurements by gamma spectrometry, the selection of counting geometry, sample properties affecting measurement accuracy, counting equipment, data analysis, etc.

Each can is equipped with an ultrasonic seal. The EURATOM Safeguards Directorate, Luxembourg, has registered the ultrasonic pattern of each seal.

Each reference sample should be handled with great care, to avoid any damage or deformation of its bottom and seal. A special transport case for the use within laboratories is supplied.

Supplementary Specifications

Can window

The uncertainties are given as maximum deviations.

- Thickness (all cans):	2.00 ± 0.02 mm
- Thickness variations within each set:	± 0.015 mm
- Deviation from flatness:	± 0.1 mm

Chemical purity of the U_3O_8

The uranium oxide is considered to be stoichiometric U_3O_8 containing impurities.

The impurities are subdivided in:

- small amounts of excess oxygen (hyperstoichiometry),
- water ($< 3200\ \mu g \cdot g^{-1}\ U_3O_8$),
- trace elements.

Their total amount for elements with $Z < 30$ is:	$< 5000\ \mu g \cdot g^{-1}$ material.
The impurity content of elements with $Z > 30$ is:	$< 10\ \mu g \cdot g^{-1}$ material.

U_3O_8 filling

The uncertainties are given as maximum deviations.

- Mass:	200.1	± 0.2 g
- Height:		
for material 031; 071; 194; 295:	20.8	± 0.5 mm
446:	15.8	± 0.5 mm
- Diameter:	70.00	$^{+\,0.05}_{-\,0.00}$ mm
- Surface density:	5.2	± 0.3 g . cm^{-2}

Uranium minor abundance isotopes

(which could interfere with the gamma-spectrometric measurements)

- $^{232}U/^{235}U$ for material	031:	$8.0 \cdot 10^{-10}$
	071:	< 0.3 "
	194:	0.3 "
	295:	0.1 "
	446:	1.0 "
- $^{233}U/^{235}U$ for all reference samples:		$< 5 \cdot 10^{-5}$
- $(^{237}U + {}^{237}Np)/^{235}U$ for all reference samples:		$< 3 \cdot 10^{-6}$

Time of chemical separation of uranium daughter products

- for material 031; 071; 194; 295:	1977
- 446:	1979

Contributors

- This NRM Project was started on the initiative of the ESARDA Working Group on Techniques and Standards for Non-Destructive Analysis. The Group advised on the elaboration of the technical specifications and its members actively participated in the execution of parts of the project.
- The U_3O_8 was supplied by British Nuclear Fuels plc, Springfields, UK.
- The cans were manufactured by NBS and CBNM.
- The reference samples were fabricated by CBNM.
- The $^{235}U/U$ abundances were determined by CBNM and NBS, as well as most of the other reference sample properties.
- The gamma spectrometry tests were performed by the CBNM, NBS and the Joint Research Centre Ispra, Italy.
- Analytical support was given by:

  Centre d'Etude Nucléaire / Studiecentrum voor Kernenergie, Mol, Belgium;

  Stichting Energieonderzoek Centrum Nederland, ECN, Petten, The Netherlands; U.S. Dept. of Energy, New Brunswick Lab., NBL, Argonne, Illinois, USA
- The ultrasonic seals were prepared by the Joint Research Centre Ispra, Italy. This action was supported by the Euratom Safeguards Directorate, Luxembourg.
- A Working Group assisted CBNM in the finalization of the EC Certification Report. Its members came from:

  Commissariat à l'Energie Atomique, CEA, Centre d'Etudes Nucléaires, CEN Saclay, France;

  Kernforschungszentrum Karlsruhe, KfK, Federal Republic of Germany;

  Stichting Energieonderzoek Centrum Nederland, ECN, Petten, The Netherlands;

  United Kingdom Atomic Energy Authority, UKAEA, Nuclear Materials Accounting Control Team, NMACT, Harwell, U.K.;

  U.S. Department of Commerce, National Bureau of Standards, NBS, Gaithersburg, MD, USA.
- The Users Manual was prepared by the Kernforschungszentrum Karlsruhe, KfK, Federal Republic of Germany.

Legal Disclaimer

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European Communities — Commission

EUR 10503 — ^{235}Uranium isotope abundance certified reference material for gamma spectrometry

EC nuclear reference material 171 certification report

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This certification report contains the information necessary for the final certification of EC nuclear reference material 171. It is also intended to inform the user of the reference material concerned on technical/scientific details which are not given in the certificate. The report describes the reference material which consists of sets of U_3O_8 samples with five different ^{235}U/U abundances, filled in cylindrical aluminium cans. The can bottom serves as window for the emitted gamma radiation.

The report describes how the ^{235}U/U abundances were characterized, how the other properties relevant for gamma measurements were determined and gives all connected results as well as those from the verification measurements. Appendix A represents the draft certificate.

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