A New Set of Uranium Isotope Reference Materials for the Improvement of Nuclear Safeguards in South America

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ABSTRACT

Uranium isotope reference materials are essential tools to provide accurate and therefore reliable measurement results of nuclear materials.

In order to improve the trust in the nuclear materials safeguards system in South America, ten materials in the form of uranium hexafluoride with isotopes amount ratios ranging from 0.5 to 20.0 % of ^{235}U in mass were recently prepared. They were enriched, purified and characterized in the Brazilian laboratories but the isotopic measurements were performed in the Institute of Reference Materials and Measurements. Modern concepts of metrology in chemical measurement were employed throughout to provide reference materials with certified values traceable to the SI and having the lowest achievable uncertainties.

Keywords: mass spectrometry, metrology in chemical measurement, nuclear safeguards, uranium isotope reference materials

1. INTRODUCTION

Modern mass spectrometry is continually enhancing its capability to provide isotope amount ratio measurement results with higher repeatability, often relying on smaller sample amounts.

This is not enough, however, to guarantee the accuracy of measurement results because there is always some kind of bias affecting the measurement process. The mass discrimination is regarded as the most important factor responsible for this bias.

The experimental values obtained are therefore corrected for mass bias by measuring certified isotope reference materials under the same instrumental conditions that were used to measure the samples.

A certified reference material is defined as a "reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certificate value is accompanied by an uncertainty at a stated level of confidence [1].

Uranium isotope reference materials have being made available to the nuclear analytical community mainly from two very well known producers, the New Brunswick Laboratory (NBL) (Chicago, USA) [2] and the Institute for Reference Materials and Measurements (IRMM) (Geel, Belgium) [3]. These two laboratories have not just the expertise but also the most advanced facilities and analytical instrumentation to produce these materials.

In spite of this, field laboratories in South America face some other hardships to accomplish their mission to provide accurate isotope ratio measurements results.

First, commercial isotope reference materials in the form of UF_6 can only be obtained in the western world from IRMM and with enrichment levels limited to 4.5 % in ^{235}U in mass.

Second, the increasing barriers presently imposed on the transportation of radioactive materials over international borders complicate the acquisition process of these essential materials.

These arguments led to the establishment of a scientific programme focused on the preparation, characterization and certification of isotope reference materials [4] under the modern concepts and practices of metrology in chemical measurement [5, 6, 7 8].

The purposes of this programme are twofold: to identify the most critical factors in the preparation and certification of these materials and to provide the Brazilian laboratories with a set of reference materials in the range of 0.5 to 20.0 % ^{235}U in mass needed to perform accurate uranium isotope ratio measurements.

2. Metrological concepts

Programmes aimed to the production of certified reference materials must necessarily be founded on sound metrological concepts because they bring consistency, quality and transparency to the certified values carried by these materials.

Metrology is defined as the "science of measurement" including all aspects both theoretical and practical with reference to measurements, wherever their uncertainty, and in whatever fields of science or technology they occur [6].

Some of the metrological concepts applied in this programme are described below.

2.1 Mesurand

The mesurand is defined as "particular quantity subjected to measurement" [6]. In this programme the isotope amount ratios, namely $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$, are considered the mesurands.

2.2 Traceability

Traceability is defined as the "property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or internationally standards, through an unbroken chain of comparisons all having declared uncertainties" [6].

The traceability of the samples to the International Systems of Units (SI) was established selecting reference materials that have the closest link to primary reference materials standing at the top of the metrological traceability chain. These materials were produced by the mixture of highly enriched uranium oxides [9, 10].

The realization of the traceability was accomplished in practice by the comparison of the isotope ratio values provided by reference materials and samples, as required by the analytical procedure.

The isotope reference materials used for this purpose are described in the tables below. The expanded uncertainty values are presented in parenthesis (k=2) after the values of the ratios.

Certified reference materials	$n(^{235}U)/n(^{238}U)$
IRMM 031	0.0032157 (16)
IRMM 071	0.0072623 (22)
IRMM 194	0.0200552 (60)
IRMM 295	0.0307711 (92)
IRMM 446	0.0473245 (14)

Table 1 Isotope amount ratio of IRMM certified reference materials

Certified reference materials	$n(^{235}U)/n(^{238}U)$
NBL U 100	0.11360 (11)
NBL U 150	0.18109 (18)
NBL U 200	0.25126 (26)

Table 2 Isotope amount ratio of NBL certified reference materials

2.3. Uncertainty estimation

The uncertainty values associated with the measured isotope amount ratios were obtained using the ISO-GUM guide [7], a comprehensive, standardized and transparent procedure for uncertainty estimation. Moreover, for practical reasons, the software GUM Workbench [11] was used to speed-up the calculations.

3. Experimental

3.1 Material preparation

Uranium hexafluoride (UF_6) was enriched to produce ten base materials with isotope ratios ranging from 0.5 to 20.0 % ^{235}U in mass.

Storage ampoules type 1S and 3S manufactured in Monel and in stainless steel respectively were cleaned, helium leak tested and conditioned with fluorine gas (F_2) prior to receiving the UF_6 samples.

Approximately 300 g of each of these base materials were distilled into ampoules 1S. They were kept at a temperature of - 80 °C in a bath of acetone and carbon dioxide to allow the light gases such as H_2, N_2, O_2 and HF to be pumped off.

The ampoules were then heated for 1 h at 150 °C, allowing the UF_6 to liquefy. They were also submitted to a vigorous shaking to provide a thorough chemical and isotopic homogenisation.

A first sub-sample with 3.0 g of UF_6 was cryogenically transferred from each ampoule 1S to an ampoule 3S to allow the isotope amount ratio measurement by gas source mass spectrometry (GSMS).

A second sub sample with 0.5 g of UF_6 was transferred cryogenically to a glass ampoule installed in a sampling system and kept a temperature of -196 °C by the immersion in liquid nitrogen.

Then, 30 mL of deionised water (18 MΩ·cm) was introduced in the glass ampoule containing UF_6 to generate uranyl fluoride according to the reaction below:

$$UF_6 + 2\ H_2O = UO_2F_2 + 4\ HF \qquad (1)$$

The uranyl fluoride solution was dried in a hot plate kept for 12 h at 60 °C to remove the existing HF. Nitric acid Suprapur 65 % 8M, manufactured by Merck (Darmstadt, Germany), was added to allow the formation of uranyl nitrate according to the following reaction:

$$UO_2F_2 + 2\ HNO_3 = UO_2\ (NO_3)_2 \cdot H_2O + 2\ HF \qquad (2)$$

The uranyl nitrate solution was then kept in a muffle for 1 h at 900 °C, enabling the formation of octauranium trioxide, as indicated below:

$$UO_2\ (NO_3)_2 \cdot H_2O = U_3O_8 \qquad (3)$$

The U_3O_8 produced was weighed, dissolved by the addition of nitric acid Suprapur 65% 8M and purified in an ion extraction column Dowex 1 x 4, 100-200 mesh manufactured by Dow Chemical (Midland, MI, USA). The eluted uranium solution was carefully dried in a hot plate.

The resulting oxide was redissolved with nitric acid generating $UO_2\ (NO_3)_2$. The solution concentration was finally adjusted to 5.0 mgU/mL, value required to run the isotope ratio measurements by thermal ionisation mass spectrometry (TIMS).

3.2 Chemical characterization

The chemical characterization of the samples consisted in the measurement of the volatile and non-volatile compounds that may be considered as impurities in UF_6 [12]. This step is important because the materials produced can be used as a reference for both chemical purity and isotopic measurements [13].

The most typical volatile impurities (HF, CoF_2, BF_3, CF_4, SiF_4, PF_5, SF_6 and WF_6) were measured by the Fourier Transformed Infrared Spectrometry (FITR) technique that allows the detection of such impurities at mg/gU levels [13].

To perform this measurement, a FTIR spectrometer, model 1750, manufactured by Perkin Elmer (Norwalk, CT, USA), was coupled to a leak tight stainless steel cell assembled with AgCl windows where the UF_6 samples to be measured were trapped.

The non-volatile compounds (twenty-four elements) were measured by inductively coupled plasma mass spectrometry (ICPMS), capable of measuring elemental concentrations at µg/gU levels[14].

An ICPMS mass spectrometer, model PQII, manufactured by Fisions (Winsford, Cheshire, England) associated to the matrix matching method was employed to perform this measurement [15].

3.3 Isotopic characterization

The isotope characterization was the most relevant task in this programme because the quantities to be certified were the isotope amount ratios $n(^{235}U)/n(^{238}U)$, $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. These data eventually allowed the calculation of the molar and the mass fraction of each sample.

As one of the main goals was the measurement of isotope ratios with the lowest achievable uncertainties, the instrumental parameters that provided the highest signal intensities in the spectrometer's ion detectors were always selected. Thus, whenever possible, Faraday detectors were chosen because they allow ion current measurements with better accuracy than the secondary electron multiplier (SEM) device.

The isotope amount ratio $n(^{235}U)/n(^{238}U)$ was measured using a MAT 511, an electron impact mass spectrometer manufactured by Varian MAT (Bremen, Germany). It is equipped with a 90° magnetic sector analyser and two fixed Faraday collectors to measure the ratio of the two major isotopes in UF_6 samples.

The measurements were carried out using the double standard method, which relies in the bracketing of the sample by two isotope reference materials (IRM). The first IRM had an isotopic ratio slightly higher and the second one an isotopic ratio slightly lower than the sample [16].

The isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were measured using the Triton, a thermal ionisation mass spectrometer manufactured by Thermo Electron (Bremen, Germany). It is equipped with a sample magazine for twenty-one filaments, 90° magnetic sector analyser, dynamic zoom optics and nine Faraday collectors, each one associated with its own signal amplifier.

For small signals the Triton also has a SEM device in combination with a retarded potential quadrupole (RPQ). This serves as an energy filter and reduces the contribution from the large ^{238}U ion beam to the much smaller ^{236}U ion beam.

The measurements were carried out mostly at the intensity of 10 V, using the modified total evaporation method in the static mode [17]. Both sample and reference materials were processed using the same operational parameters.

The measurement of the minor isotope ratios for some samples of the set employed a different method [18], where the ^{238}U ion beam was kept at the highest possible intensity, typically 30V.

In the samples where the isotope ratio $n(^{236}U)/n(^{238}U)$ was smaller than 10^{-5}, the SEM device was employed. The ^{234}U ion beam was then used to run the inter-calibration routine between the SEM and the *Faraday/ multi-collector*.

The GSMS and TIMS techniques described above were selected to be employed in this programme because comparative studies with other techniques demonstrated they were capable to provide the smallest achievable uncertainties for uranium [19].

4. Results and discussion

4.1 Chemical characterization results

The measured concentrations of volatile impurities are presented in table 3 for a group of three samples, representative of the categories of natural, enriched and depleted materials in ^{235}U.

Volatile impurities	MRI 0.5	MRI 0.7	MRI 2.5
	mg/100g	mg/100g	mg/100g
HF	4.7 ± 0.5	4.5 ± 0.5	4.6 ± 0.5
CF_4	0.004 ± 0.002	0.003 ± 0.002	0.006 ± 0.002
SiF_4	0.003 ± 0.002	0.004 ± 0.002	0.005 ± 0.002

Table 3 Concentrations of volatile impurities in UF_6 samples

The volatile impurity detected in the highest concentration was the HF, formed by the decomposition of UF_6 in the presence of air humidity. This gas can be easily removed by high vacuum pumping if the ampoules are kept at temperatures below - 80 ^{0}C.

The infrared spectrum of sample MRI 2.5 is presented in figure 1. The wavelength (cm^{-1}) is presented in the abscissa, while the transmittance (T%) is in the ordinate. The peaks featured at the right of the spectrum are those associated with the UF_6 (677 cm^{-1}) while the peaks at the left are associated with the HF (4 039 cm^{-1}). No other impurities were identified in this spectrum.

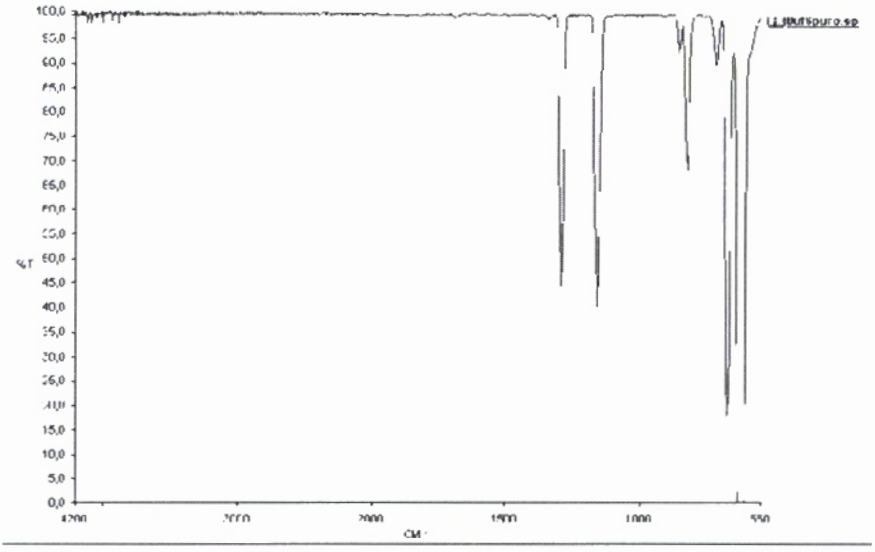


Figure 1 Spectrum of sample MRI 2.5 measured by Fourier Transformed Infrared Spectrometry (FTIR)

The sum of the measured concentration of twenty-four elements (Be, B, Na, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ag, Cd, Sn, W, Pb, Bi) plus eighteen rare-earth elements (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf and Th) is presented in table 4.

Non-volatile impurities	MRI 0.5	MRI 0.7	MRI 2.5
	µg/g	µg/g	µg/g
Total	152 ± 24	158 ± 24	185 ± 24

Table 4 Concentrations of non-volatile impurities in UF_6 samples

Tables 3 and 4 show the samples have a total impurity concentration lower than 5.0 mg in 100 g of sample, which results in a purity level of 99.995 %. In this way the material can be considered sufficiently pure to be used as isotopic reference materials in the most demanding measurement processes.

4.2 Isotopic characterization results

The measurement results for the isotope amount ratio $n(^{235}U)/n(^{238}U)$ are presented in table 5. The absolute values of expanded uncertainty (U), calculated with coverage factor (k) equal to 2, are presented between parentheses after the isotope ratios. Their relative values (%) are presented in a separated column.

MRI	$n(^{235}U)/n(^{238}U)$	U (k=2)
		%
0.5	0.005 354 7 (17)	0.032
0.7	0.007 254 3 (16)	0.022
1.0	0.010 370 3 (18)	0.017
2.5	0.024 232 0 (42)	0.017
3.5	0.035 469 8 (47)	0.013
4.5	0.046 545 7 (65)	0.014
6.5	0.069 850 (23)	0.033
10	0.107 545 (90)	0.084
15	0.182 38 (18)	0.10
20	0.254 42 (28)	0.11

Table 5 Results of isotope amount ratio $n(^{235}U)/n(^{238}U)$ and expanded uncertainties (U) obtained by GSMS technique

Table 5 shows that the relative expanded uncertainty values for all samples are lower than 0.11 % and seven samples of the set have uncertainties even lower than 0.05 %. This is remarkable achievement because the expanded uncertainty estimated according to the ISO-GUM is a quantification of the reliability of the measurement performed.

The uncertainties of samples MRI 10, 15 and 20 are three to four times higher than the others in the set. This is due to the need to use isotope reference materials for these three samples with higher expanded uncertainties than those used for the remaining samples.

The analysis of the uncertainty budget of each sample revealed that the standard uncertainty is composed by two main components: the uncertainty of the isotope reference materials used and the repeatability of measurements required by the analytical method employed.

As the dominant component in the budget is the first one, the increase in the uncertainty of the reference materials used in the measurement process implies an increase in the uncertainties of the three mentioned samples.

The relative contributions of these two components to the standard uncertainty (k=1) of the isotope ratio of sample MRI 2.5 is presented in figure 2.

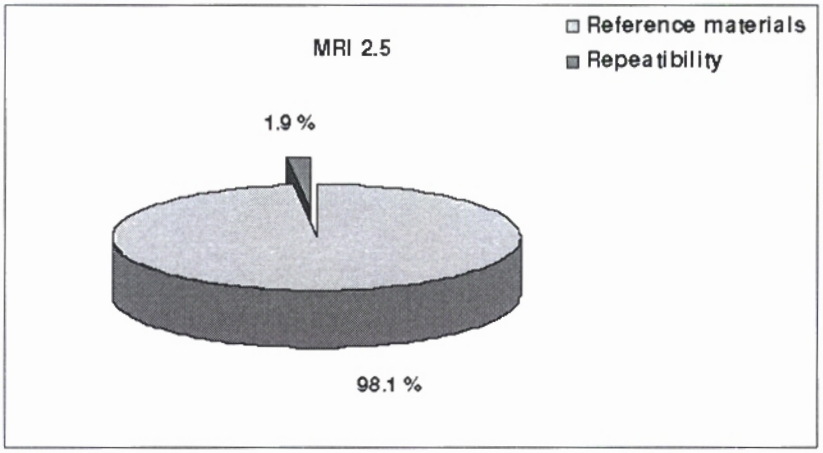


Figure 2 Relative contribution of the components to the standard uncertainty of the isotope amount ratio $n(^{235}U)/n(^{238}U)$ for sample MRI 2 5 measured by GSMS

The measurement results for the isotope ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ are presented in table 6.

MRI	$n(^{234}U)/n(^{238}U)$	U %	$n(^{236}U)/n(^{238}U)$	U %
0.5	$3.581\,2\cdot10^{-5}$ (45)	0.13	$1.148\,0\cdot10^{-6}$ (32)	0.28
0.7	$5.658\,1\cdot10^{-5}$ (41)	0.07	$3.213\,3\cdot10^{-8}$ (89)	0.28
1.0	$8.70\cdot10^{-5}$ (10)	1.15	$2.917\cdot10^{-6}$ (40)	1.37
2.5	$2.092\,8\cdot10^{-4}$ (13)	0.06	$1.140\,8\cdot10^{-7}$ (31)	0.27
3.5	$3.327\,1\cdot10^{-4}$ (18)	0.05	$3.881\,0\cdot10^{-4}$ (11)	0.03
4.5	$4.411\cdot10^{-4}$ (98)	2.22	$5.44\cdot10^{-4}$ (12)	2.21
6.5	$8.725\cdot10^{-4}$ (78)	0.90	$1.697\cdot10^{-4}$ (20)	1.18
10	$1.032\,2\cdot10^{-3}$ (67)	0.65	$9.90\cdot10^{-4}$ (14)	1.40
15	$1.744\,4\cdot10^{-3}$ (44)	0.25	$1.695\,5\cdot10^{-3}$ (59)	0.35
20	$2.404\,4\cdot10^{-3}$ (12)	0.05	$2.323\,39\cdot10^{-3}$ (59)	0.03

Table 6 Results of the isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ and expanded uncertainties obtained by TIMS technique

Although all samples were initially measured using a Finnigan MAT 262 mass spectrometer, the most representative and therefore important samples of the set (MRI 0.5, 0.7, 2.5, 3.5 and 20) were re-measured using a Finnigan Triton, a mass spectrometer having more powerful measuring resources.

The measurement results from both instrumentations were in close agreement and must be considered statistically equivalent if their expanded uncertainties are taken into account. Yet the results provided by the Triton always presented lower uncertainty values as can be seen in table 6.

The analysis of the uncertainty budget for isotope amount ratio $n(^{234}U)/n(^{238}U)$ revealed that the isotope reference materials used and the repeatability have varying contributions depending on the ^{234}U concentration in the sample.

The relative contributions obtained for sample MRI 2.5 are presented in figure 3 as an example

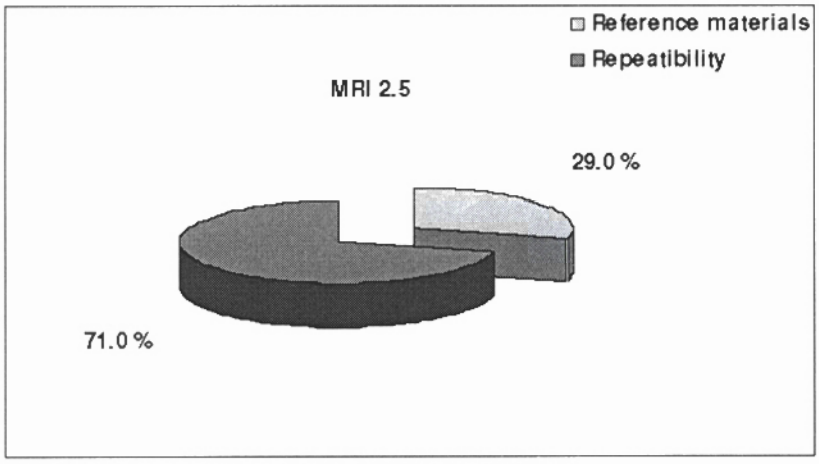


Figure 3 Relative contribution of the components to the standard uncertainty of the isotope amount ratio $n(^{234}U)/n(^{238}U)$ for sample MRI 2.5 measured by TIMS-Triton

Analysis of the uncertainty budget of the isotope amount ratio $n(^{236}U)/n(^{238}U)$, presented in figure 4, revealed that a significant uncertainty is introduced from the need to calibrate the SEM device. Should this component be neglected, the value of the total uncertainty would be seriously underestimated.

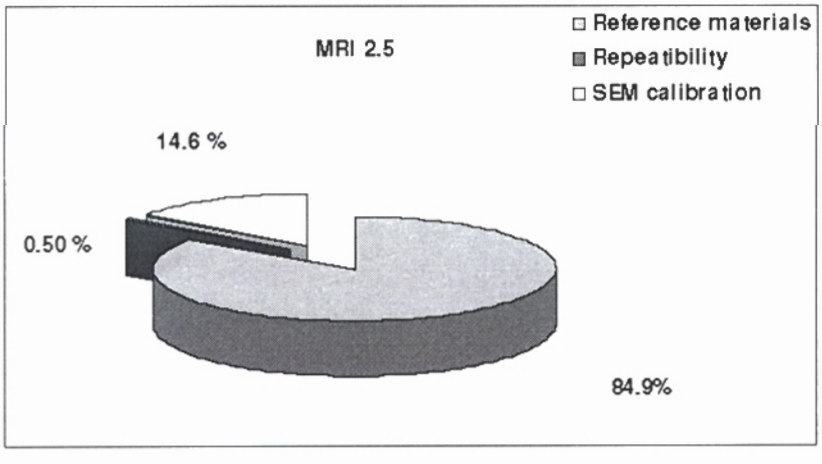


Figure 4 Relative contribution of the components to the standard uncertainty of the isotope amount ratio $n(^{236}U)/n(^{238}U)$ for sample MRI 2.5 measured by TIMS-Triton

4.3 Sample stability, homogeneity and storage

Material stability was not a matter of concern in this programme because UF_6 is stable up to 1 000 K.

However, the compound it is extremely reactive, especially when in contact with water. It must therefore be stored in stainless steel ampoules, assembled with high vacuum valves and helium leak tested.

At the end of the experimental part of this programme, the UF_6 samples stored in ampoules 1S were homogenised for 1 h at 90 C and then transferred to ampoules 3S. A final measurement confirmed the thorough isotopic homogeneity in each ampoule.

The ampoules 1S (larger one) and 3S (smaller one) containing the isotope reference material MRI 2.5 can be seen in figure 5.

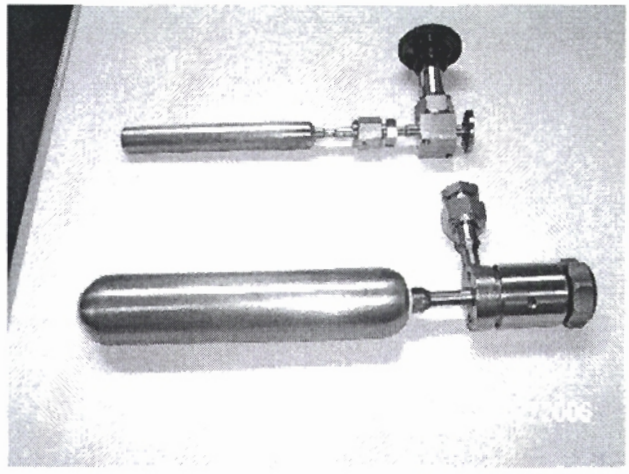


Figure 5 Ampoules 1S and 3S used to store isotope reference materials MRI 2.5

4.4 Certification of the isotope reference materials produced

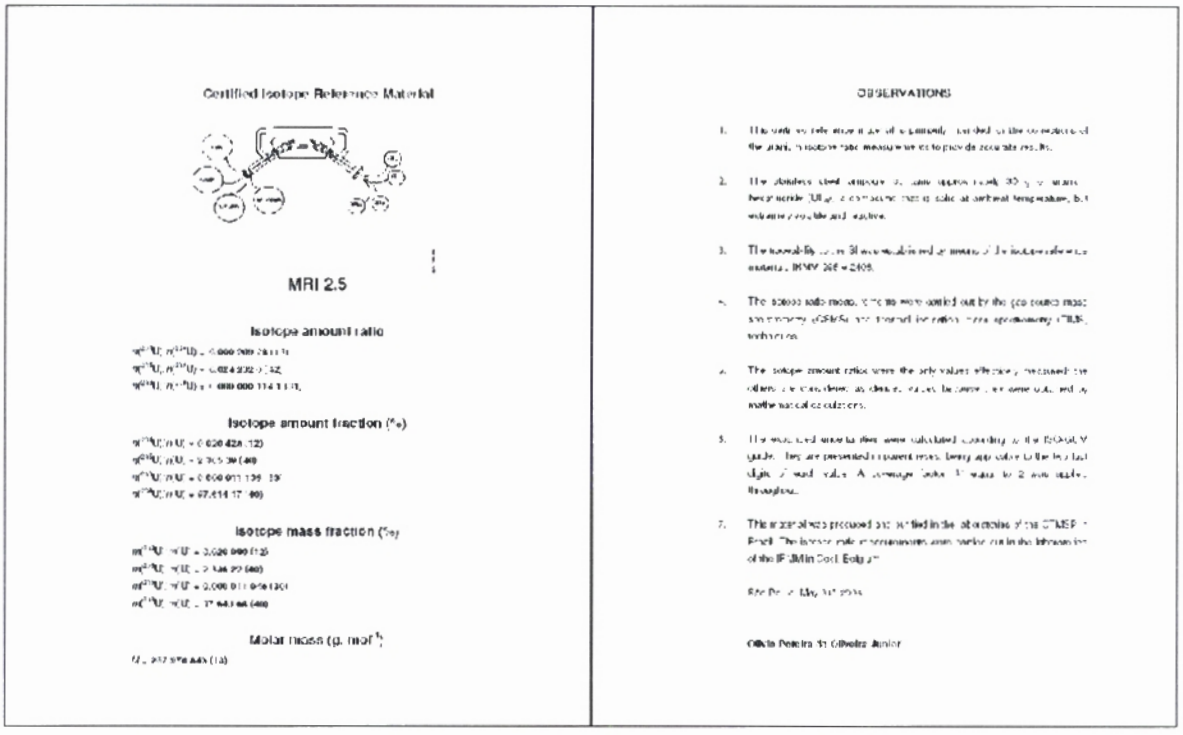
The certificate associated to each material produced brings its official code number, the measured isotope amount ratio and other very important analytical data like its isotope amount fraction, isotope mass fraction and molar mass.

These last values are considered derived values because they were calculated from the measured isotope amount ratios presented in tables 5 and 6.

The intended use of the material, the amount of UF_6 within the ampoule, the particular traceability link to the SI and other valuable information are also written in the certificate.

The definition of an expiry date was deemed not applicable for this kind of material.

The official certificate of the Isotope Reference Material MRI 2.5 is presented in figure 6 as an example.



Certified Isotope Reference Material

MRI 2.5

Isotope amount ratio

Isotope amount fraction (%)

Isotope mass fraction (%)

Molar mass (g mol^{-1})

OBSERVATIONS

1.

2.

3.

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Otávio Pereira Silveira Júnior

Figure 6 Certificate of the Isotope Reference Material MRI 2.5

5. Conclusions

A set of ten UF_6 isotope reference materials in the range of 0.5 to 20.0 % ^{235}U in mass were successfully prepared, purified, characterized and certified.

These samples are traceable to the SI because isotope reference materials ultimately linked to synthetic mixture of highly enriched oxides were employed in the measurement process.

The measurement uncertainties of the isotope ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{238}U)/n(^{238}U)$ are in the range of de 0.05 to 2.22 %, 0.013 to 0.10 % and 0.03 to 2.21 % respectively.

This set of materials will be used not just in the measurement process of ordinary samples, but also in the calibration of mass spectrometers, quality control routines and evaluation of the performance of new instruments, methods and techniques.

The utilization of these materials will eventually allow the achievement of isotope amount ratios associated with much lower uncertainty values for the safeguards samples processed in Brazilian laboratories.

Consequently it will contribute to the improvement of the reliability and trust of the nuclear material safeguards system in South America.

This paper is dedicated to Dr. Roger Wellum on the occasion of his retirement

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