ESTABLISHING THE METROLOGICAL TRACEABILITY TO THE SI OF THE URANIUM ISOTOPE REFERENCE MATERIALS PREPARED IN BRAZIL

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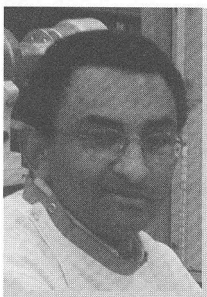


Olivio Pereira de Oliveira Junior graduated as chemical engineer at the Escola Politecnica da Universidade de São Paulo (USP) in 1982. He immediately joined the Instituto de Pesquisas Energeticas e Nucleares (IPEN) to work in the field of vacuum technology. Then he was involved with leak detection techniques for materials quality evaluation. In this field he was certified as American Society for Non Destructive Testing (ASNT) Level III inspector. Later on he was involved with the calibration of low-pressure capacitance manometers and UF_6 gas flowmeters used in uranium isotope enrichment installations. He got his Masters degree at USP in 2000 dealing with multielemental and isotope ratio measurements by ICPMS. In 2000 and 2001 he was fellow of the International Atomic Energy Agency (IAEA) in Vienna to study the requirements of the nuclear safeguards system. From 2002 to 2005 he worked as a detached national expert at the Institute for Reference Materials and Measurements (IRMM) in Belgium. He got his PHD at USP in 2006 dealing with the preparation, characterization and certification of uranium isotope reference materials.

Abstract – *The establishment of the metrological traceability to a stated reference is a basic requirement for the certification process of reference materials. This important issue was addressed in a programme aimed to the preparation, characterization and certification of uranium isotope reference materials in Brazil. The metrological traceability was accomplished in practice using the power of high precision gas source mass spectrometry performed at the IRMM to compare the isotope amount ratios in the Brazilian materials to the ratios of materials certified by the use of synthetic mixtures of highly enriched uranium oxides. The isotope ratios in these mixtures were determined by gravimetry, a primary method of measurement, which enabled a direct link to the International System of Units (SI). The definitions and concepts of the newest edition of the VIM were adopted in this paper.*

Key-words: *metrological traceability, uncertainty, uranium isotope reference materials.*

Introduction

Certified uranium isotope reference materials are analytical tools used whenever accurate measurement results of isotope amount ratios are needed. This is the case of measurements for nuclear fuel characterization or nuclear materials safeguards.

The definition of a certified reference material involves two concepts that are closely linked: metrological traceability and measurement uncertainty [1]. They were addressed in a programme focused in the preparation, characterization and

certification of isotope reference materials in the form of uranium hexafluoride (UF_6), ranged from 0.5 to 20.0% ^{235}U in mass [2].

Samples were enriched and chemically characterized in Brazil but the isotope amount ratio measurements were carried out at the Isotope Measurements Unit (IM) of the Institute for Reference Materials and Measurements (IRMM) [3].

The aim of this paper is twofold: to present how the metrological traceability to the SI was established and the magnitude of the measurement uncertainties associated with the uranium isotope amount ratios of the Brazilian materials.

Metrological concepts applied

Metrology is defined as the "science of measurement and its application". It includes all theoretical and practical aspects of measurement, whatever the measurement uncertainty and field of application [4].

Hence any activity involved with the production of certified reference materials must be founded in sound scientific concepts to allow the use of these materials in the most stringent analytical measurements.

The concepts of mesurand, metrological traceability and measurement uncertainty were the most important in this programme and are described below.

Measurand

The measurand is defined as "quantity intended to be measured" [4]. 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 measurands although just the $n(^{235}U)/n(^{238}U)$ measurement results will be presented in this paper.

Metrological traceability

The metrological traceability is defined as the "property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty" [4].

The traceability to the SI of the set of reference materials produced in Brazil was not calculated but established even before the start of the experimental measurements. It was accomplished via the use of certified reference materials produced by the IRMM.

These IRMM reference materials were prepared in this way: five batches of U_3O_8 with about 30 kg each were purified, homogenised and characterized [5]. Their isotope amount ratios were measured by gas source mass spectrometry (GSMS) using the double standard method. This measuring method relies on two primary reference materials; the first one must have an isotope amount ratio slightly higher and the other a ratio slightly lower than the ratio of each batch [6].

The preparation of these primary reference materials was carried out using the synthetic isotopic mixtures, method proposed by Nier and improved over the years.

This method ultimately relies on gravimetry, recognised by the Comité Consultatif pour la Quantité de Matière (CCQM) as a primary method of measurement because its operation can be completed described and understood, and

for which a complete uncertainty statement can be written down in terms of SI units [7].

Each primary reference material was prepared in the following way: two samples of pure U_3O_8, with approximately 3 g each, highly enriched (99.9%), the first just in ^{235}U, and the second just in ^{238}U were calcinated together at 900 °C to assure the same stechiometry. Then, the samples were weighed very carefully to get the lowest measurement uncertainty. Finally they were mixed and homogenised.

The isotope amount ratio $n(^{235}U)/n(^{238}U)$ in the mixture was calculated using the equation 1, where the only experimental values are the masses of the two samples.

$$n(^{235}U)/n(^{238}U) = \frac{n(^{235}U)}{n(^{238}U)} = \frac{[m(^{235}U)/(M\,^{235}U)]}{[m(^{238}U)/(M\,^{238}U)]} \qquad (1)$$

where,

$n(^{235}U)/n(^{238}U)$ = isotope amount ratio of the isotopes ^{235}U e ^{238}U
$n\,(^{235}U)$ = amount of isotope ^{235}U
$n\,(^{238}U)$ = amount of isotope ^{238}U
$m(^{235}U)$ = mass of the isotope ^{235}U in the sample (g)
$m\,(^{238}U)$ = mass of the isotope ^{238}U in the sample (g)
$M(^{235}U)$ = molar mass of the isotope ^{235}U (g/mol)
$M(^{238}U)$ = molar mass of the isotope ^{238}U (g/mol)

The output quantity in the equation 1 is a ratio of amounts so that the result is directly traceable to the SI unit, mole. This method is a primary method of measurement because it links the realisation of the unity directly to the definition of the unit.

The values of the primary reference materials determined according to equation 1 are presented in table 1.

Table 1 – Isotope amount ratio of primary reference materials.

Primary reference materials	$n(^{235}U)/n(^{238}U)$ k = 2	U(k = 2) %
82	0.00321019 (41)	0.01
83	0.00324159 (41)	0.01
118	0.00720669 (61)	0.01
119	0.00732601 (62)	0.01
102	0.0201836 (18)	0.01
103	0.0199767 (21)	0.01
104	0.0305990 (32)	0.01
105	0.0309820 (32)	0.01
106	0.0471216 (47)	0.01
107	0.0475467 (48)	0.01

It is important to note that the relative expanded measurement uncertainties in this set of materials is limited to 0.01%, the lowest reachable value for this kind of materials.

Unfortunately the cost of highly enriched uranium oxides prevented the preparation of larger amounts of these materials.

The measurement results of the isotope amount ratio $n(^{235}U)/n(^{238}U)$ for the five batches are presented in table 2. The expanded measurement uncertainty is quoted in parenthesis with a coverage factor equal to 2, so as to have a level of confidence level of approximately 95%.

Table 2 – Isotope amount ratio of IRMM certified reference materials.

Certified reference materials	$n(^{235}U)/n(^{238}U)$ k = 2	U(k = 2) %
IRMM 031	0.0032157 (16)	0.050
IRMM 071	0.0072623 (17)	0.023
IRMM 194	0.0200552 (38)	0.019
IRMM 295	0.0307711 (51)	0.017
IRMM 446	0.0473248 (82)	0.017

The reference materials listed in table 2 have isotope amount ratio results directly traceable to the results of the primary reference materials listed in table 1. Therefore they can be considered as certified reference materials.

The materials produced in Brazil will have measurement results traceable to the results of the certified reference materials listed in table 2. As a consequence, they can also be considered certified reference materials.

Thus, the metrological traceability chain for the Brazilian materials MRI 0.5, 0.7, 1.0, 2.5, 3.5, 4.5 and 6.5 is easily established and is presented in figure 1.

Because there are no IRMM reference materials with isotope amount ratios higher than 0.047325, the metrological traceability to the SI for the Brazilian materials with higher ratios was accomplished using the reference materials produced by the New Brunswick Laboratory (NBL) [8]. These materials are presented in table 3.

Table 3 – Isotope amount ratio of NBL certified reference materials.

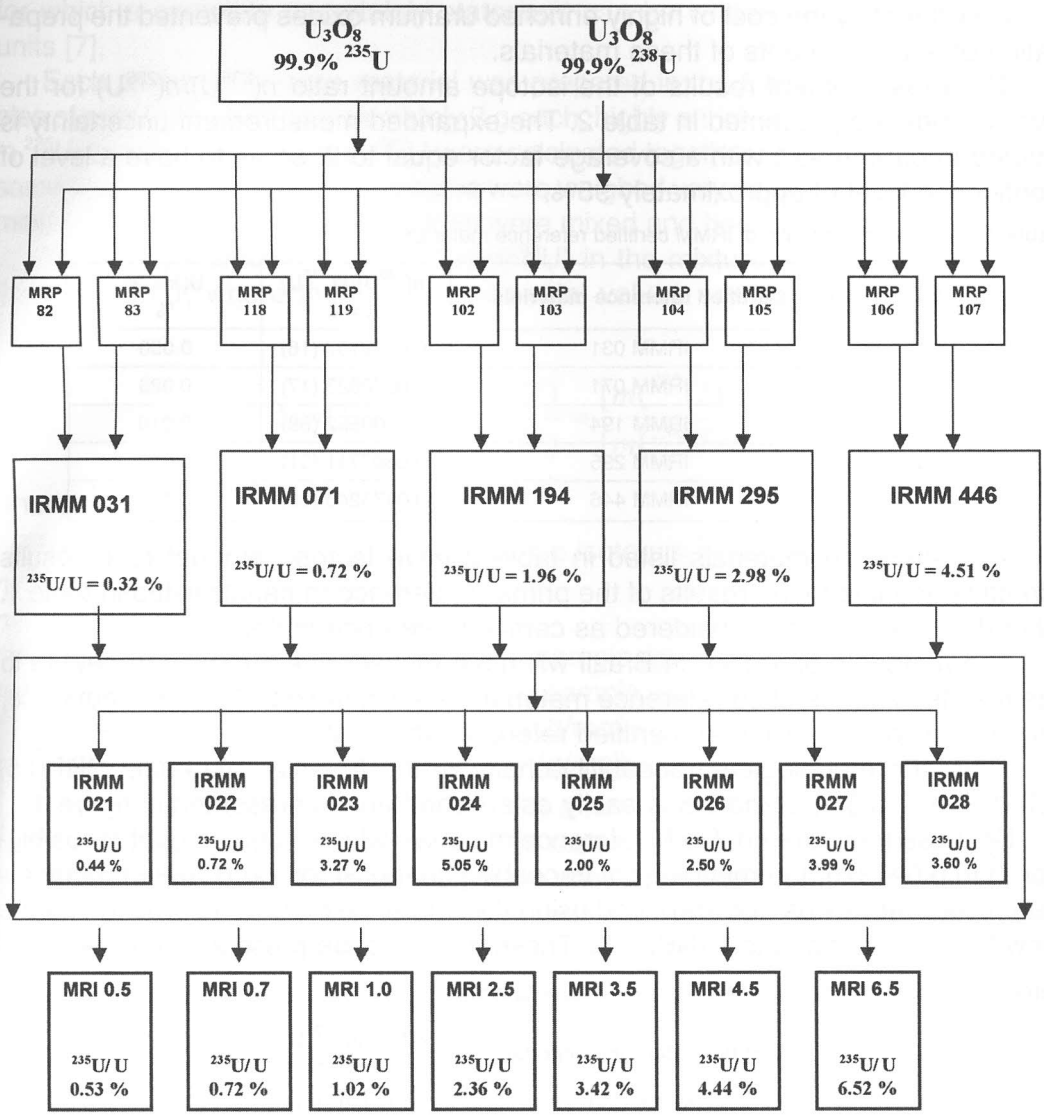
Certified reference materials	$n(^{235}U)/n(^{238}U)$ k = 2	U(k = 2) %
NBL U 100	0.11360 (11)	0.10
NBL U 150	0.18109 (18)	0.10
NBL U 200	0.25126 (26)	0.10

Measurement uncertainty

The BIPM-ISO-GUM [9] was identified as the best guide to estimate the measurement uncertainties associated with the isotope amount ratios. To facilitate the calculations, the dedicated software GUM Workbench was used throughout this work [10].

Metrological hierarchy

Certified reference materials	Identification
Primary	82, 83, 118, 119, 102, 103, 104, 105, 106, 107
Secondary	IRMM 031, 071, 194, 295, 446



Secondary IRMM 021, 022, 023, 024, 025, 026, 026, 028
Secondary IRMM 0.5, 0.7, 1.0, 2.5, 3.5, 4.5, 6.5

Figure 1 – Metrological traceability chain for uranium samples.

Experimental

Uranium hexafluoride (UF_6) samples were enriched in a Brazilian centrifuge facility to produce ten base materials with isotope ratios ranging from 0.5 to 20.0% ^{235}U in mass. These materials were stored in stainless steel ampoules that have been cleaned, helium leak tested and conditioned with fluorine gas (F_2) prior to receiving the UF_6 samples.

The materials were heated at 150°C for 1h and submitted to a vigorous mechanical shaking to provide a full chemical and isotopic homogenisation. Then

they were submitted to a chemical characterization process to measure the volatile and non-volatile elements regarded as impurities in UF_6.

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

The establishment of the metrological traceability chain was carried out in practice comparing the $n(^{235}U)/n(^{238}U)$ isotope amount ratio values measured in the IRMM (table 2) or NBL (table 3) reference materials (known ratios) to the ratios measured in the Brazilian samples (unknown ratios), as required by the double standard measuring method.

Results and discussion

The measurement results for the isotope amount ratio $n(^{235}U)/n(^{238}U)$ of the Brazilian reference materials are presented in table 4.

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.

Table 4 – Isotope amount ratios of Brazilian certified reference materials

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

The measurement results presented in table 4 can be divided into two groups. The first group is comprised by materials MRI 0.5, 0.7, 1.0, 2.5, 3.5, 4.5 and 6.5. They were measured using IRMM reference materials and provided uncertainty values in the range of 0.013 to 0.033%.

The second group is formed by materials MRI 10, 15 and 20. They were measured using NBL reference materials, which resulted in uncertainty values in the range of 0.084 to 0.011%.

These differences in the uncertainty levels of the Brazilian materials are due to the fact that IRMM reference materials have lower uncertainty values than NBL materials.

In both cases, the use of the method based on the comparison of isotope ratios did not increase significantly the uncertainty in the Brazilian materials. Indeed, the expanded uncertainty values of these materials were very close to the uncertainty of the certified reference materials actually used in the measurement process.

This is a demonstration of the power of the high precision gas source mass spectrometry to establish the trace between certified reference material and sample without compromising the uncertainty levels.

The hierarchy of the certified reference materials involved in this programme can be described in this way: the materials listed in table 1 are the only primary reference material in this field; the materials listed in tables 2, 3 e 4 are secondary reference materials because they make reference to primary reference materials in some point of their metrological traceability chain.

Conclusions

The metrological traceability to the SI of the uranium isotope reference materials prepared in Brazil was successfully established.

Once this requirement was met, the use of these materials in any measurement process can provide results that can be metrologically compared to any other result obtained elsewhere in space and time.

The uncertainty levels associated with the $n(^{235}U)/n(^{238}U)$ isotope amount ratio in the set of Brazilian materials were in the range of 0.013 to 0.11%. These values are good enough for isotope amount ratio measurements performed for nuclear fuel characterization or nuclear materials safeguards.

The Brazilian uranium certified isotope reference materials have been in use in our nuclear laboratories for more than a year improving the reliability of uranium isotope amount ratio measurements performed in the country.

The preparation and certification of these reference materials is therefore a contribution to a better management of the nuclear material in Brazil.

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