Hungary

BudaPest

ESARDA 2011

ESARDA
European SAfeguards Research and Development Association

33rd ESARDA Annual Meeting

Symposium on safeguards and nuclear material management
May 16-20, 2011 Budapest, Hungary

ABSTRACTS

18026

18026

Verification of the reliability of the certified isotope reference materials prepared for nuclear safeguards

Olívio Pereira de Oliveira Junior

Instituto de Pesquisas Energéticas e Nucleares (IPEN)
Av. Lineu Prestes 2242, Cidade Universitária, Butantã,
05508-000 São Paulo, SP, Brazil
E-mail: oliviojr@ipen.br

Centro Tecnológico da Marinha em São Paulo (CTMSP)
05508-000 São Paulo, SP, Brazil

ABSTRACT

A set of isotope reference materials in the form of uranium hexafluoride ranging from 0.5 to 20.0 % of ^{235}U in mass was prepared and made officially available to Brazilian nuclear analytical laboratories.

The use of these materials in the measurement process of blind samples received in the frame of an international interlaboratory comparison program was regarded as an excellent opportunity to independently verify their reliability.

The compliance of the combined uncertainties associated with the $n(^{235}U)/n(^{238}U)$ isotope amount ratios measured in depleted, natural and low-enriched uranium and the IAEA International Target Values 2010 confirmed the accuracy of the certified isotope amount ratios and therefore demonstrated the reliability of the prepared isotope reference materials.

Keywords: uranium isotope amount ratios, certified reference materials, mass spectrometry, interlaboratory comparison program, metrology in chemistry

1. INTRODUCTION

Mass spectrometry has long been recognised as the most traditional technique to measure isotope amount ratios. It is able to provide measurement results with high repeatability, just requiring small sample amounts.

There are several mass spectrometry techniques available due to the combination of different ions sources, mass analysers and ion detectors.

These techniques are very precise but this is not enough to guarantee the accuracy of measurement results because is always some kind of bias affecting the measurement process.

Mass discrimination is regarded as the most important factor responsible for this bias. It is corrected by the use of certified isotope reference materials (IRM) under the same instrumental conditions that were used to measure the samples.

According to VIM 2008 3rd edition[1], a certified reference material is defined as a "reference material, accompanied by a documentation, issued by a authoritative body, and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures".

Certified IRM can also be used to calibrate mass spectrometers, evaluate analytical techniques and methods and set the reference values in interlaboratory comparison (ILC) of measurement results.

Uranium certified IRM have been produced by few top laboratories in the world, the New Brunswick Laboratory (NBL-DOE-USA) (Chicago, USA) [2] and the European Commission Institute for Reference Materials and Measurements (IRMM-JRC-EU) (Geel, Belgium) [3].

Nevertheless, isotope reference materials in the form of UF_6 can only be obtained in from IRMM and with enrichment levels limited to 4.5 % in ^{235}U in mass. Besides, the increasing barriers presently imposed on the transportation of radioactive materials over international borders are complicating the acquisition process of these materials.

These facts led to the establishment of a scientific programme in Brazil focused on the preparation, characterization and certification of uranium isotope reference materials under the modern concepts and practices of metrology in chemical measurement [4].

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. These materials were then distilled, homogenised and sampled.

The chemical measurements required to assess the purity of these materials were performed in Brazil, at CTMSP laboratories. Volatile impurities in UF_6 were measured by Fourier Transformed Infra-Red Spectrometry (FTIR) and the non-volatile impurities by a quadrupole Inductively Coupled Plasma Mass Spectrometry (ICPMS) using the matrix-matched method [5].

The measurements required to certify the isotope amount ratios of these materials were performed at IRMM laboratories using three independent techniques: Gas Source Mass Spectrometry (GSMS), Thermoionisation Mass Spectrometry (TIMS) and Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS). The details of this programme is published elsewhere [6,7,8].

2. OBJECTIVES

The objectives of this work are twofold:

(a) to verify the accuracy of the isotope amount ratios of some of the Brazilian IRM produced,
(b) to check the compliance of the uncertainties associated with the $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratio measurements carried out at CTMSP with the requirements of the IAEA International Target Values 2010 for Measurement Uncertainty in Safeguarding Nuclear Materials[9].

The participation in an international interlaboratory comparison of measurement results was deemed as an excellent opportunity to execute these two tasks. This intent was realized in fiscal year 2010, in the framework of the "Safeguards Measurement Evaluation Program (SMEP)" organised by NBL.

3. Experimental

3.1 UF_6 samples

NBL sent to CTMSP eight (8) UF_6 samples with isotope ratios ranging from 0.5 to 4.5 % ^{235}U in mass. The identification and approximate ^{235}U (%) content in mass of these samples are presented in table 1. Half of these samples were analysed in the 2nd quarter and half in the 4th quarter of the year.

SMEP Ampoule	^{235}U (%)
J 68	0.5
J 69	0.5
J 168	1.3
J 169	1.3
J 268	3.0
J 269	3.0
J 371	5.0
J 373	5.0

Table 1 Approximate content of ^{235}U (%) in mass

The received UF_6 samples from NBL were stored in PT-10 Teflon ampoules, sealed with a Teflon disks and metal connections. Firstly they were cooled in liquid nitrogen at -196 ^{0}C and then opened, to allow the installation of metal valves to facilitate the required measurement operations. Then they were kept at a temperature of - 80 ^{0}C in acetone and carbon dioxide bath to allow the light gases such as H_2, N_2, O_2 and especially HF to be pumped off.

3.2 Isotopic measurement

The isotope amount ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were measured in all samples. Nevertheless, just the results of the $n(^{235}U)/n(^{238}U)$ will be presented in this work.

The mass spectrometer used was the IMU 200, manufactured by IPI Instruments (Bremen, Germany). It is equipped with an electron impact ion source, quadrupole mass analyser, one Faraday detector and one secondary electron multiplier (SEM), device that allows the measurement of low ion signals.

The measurements were carried out using the single standard method. In this method it is very important to select a certified IRM whose isotopic ratio is as close as possible to that of the sample.

It is noteworthy that just the Brazilian IRM were be used in this work.

4. Results and discussion

The results for the isotope amount ratio $n(^{235}U)/n(^{238}U)$ for all samples are presented in table 2. The systematic (u_s) and the random (u_r) components of the uncertainty are presented as well as the value of the combined uncertainty (u_c).

Parameter	J68 & J69	J168 & J169	J268 & J269	J371 & J373
Number of measurements per day	6	6	6	6
Total number of measurements	12	12	12	12
Mean of measured results	0.53727	1.29190	2.98624	4.7959
SD	0.00020	0.00040	0.00061	0.00091
RSD (%)	0.04	0.03	0.02	0.02
Certified value (%)	0.53707	1.2919	2.9843	4.7924
u_s	0.04	0.00	0.07	0.07
u_r	0.006	0.03	0.018	0.026
u_c	0.04	0.03	0.07	0.07

Table 2 Results of $n(^{235}U)/n(^{238}U)$ isotope ratio measurements, certified isotope ratio, systematic, random, and combined uncertainty components.

The data presented in table 2 shows that the repeatability values obtained for all 8 samples, expressed in terms of relative standard deviation (RSD) were in the range of 0.02 to 0.04%. This is a very good result, confirming the high stability ion signal provided by the electron impact ion source of this instrument.

The systematic uncertainties (bias) were in the range of 0.04 to 0.07 %, which is an excellent result for a quadrupole based instrument.

The requirements of the ITV 2010 for several categories of nuclear materials and analytical methods are presented in table 3.

Method	Category	Uncertainty components		
		u_r	u_r	u_c
GSMS	DUF_6 & NUF_6	0.1	0.1	0.14
	$LEUF_6$	0.05	0.05	0.07
TIMS	DU (< 0.3 ^{235}U)	0.5	0.5	0.7
MC ICPMS	U (0.3 %< ^{235}U< 1.0 %)	0.2	0.2	0.28
	LEU (1% < ^{235}U< 20 %)	0.1	0.1	0.14
	HEU (> 20%)	0.05	0.05	0.07

Table 3 Requirements of the IAEA International Target Values 2010 for Measurement Uncertainties for Safeguarding Nuclear Materials

The comparison between the combined uncertainties associated to the $n(^{235}U)/n(^{238}U)$ isotope ratios measured in the set of samples and the requirements of the ITV 2010 is presented in table 4.

	J68 & J69	J168 & J169	J268 & J269	J371 & J373
Category of the material	DU	U	LEU	LEU
ITV 2010 (%)	0.14	0.14	0.07	0.07
Obtained combined uncertainty (%)	0.04	0.03	0.07	0.07

Table 4 Comparison between the requirements of the ITV 2010 and the obtained values for the combined uncertainty for the set of samples of the NBL SMEP 2010

The data presented in table 4 shows that the requirements of ITV 2010 document were met for all three categories of materials: depleted uranium (DU), natural uranium (U) and low enriched uranium (LEU).

This achievement was only possible for two reasons. First, the mass spectrometer used provided results with high repeatability. Second, the Brazilian isotope reference materials have accurate ratios, which allowed a very good correction of the observed isotope amount ratios.

5. Conclusions

The Brazilian isotope reference materials used in this work do have accurate isotope amount ratios as demonstrated by the results of the participation in the NBL Safeguards Measurement Evaluation Program (SMEP) 2010.

The requirements of the IAEA ITV 2010 were met for three categories of nuclear materials: depleted, natural and low-enriched when the Brazilian isotope reference materials were in use.

The Brazilian isotope reference materials are reliable and therefore can be used to measure safeguards samples. This result certainly contributes to build a trustful nuclear safeguards system in South America.

6. References

[1] International Vocabulary of Metrology – Basic and General Concepts and Associated Terms, JCGM 200:2008, Bureau International des Poids et Mesures (BIPM).

[2] New Brunswick Laboratory (NBL), U.S. Department of Energy, Argonne, Illinois, USA, http://www.nbl.doe.gov

[3] Institute for Reference Materials and Measurements (IRMM), Joint Research Center (JRC), European Commission (EC), Geel, Belgium, http://www.irmm.jrc.be

[4] Pereira de Oliveira Junior, O., Preparation, Characterization and Certification of Uranium Isotopic Reference Materials, PHD thesis presented at the University of São Paulo, São Paulo, Brazil, July 2006, http://www.teses.usp.br/teses

[5] Pereira de Oliveira Junior, O. and Sarkis, J. E. S., Determination of Impurities in Uranium Samples by Inductively Coupled Plasma Mass Spectrometry using the Matrix Matched Method , J. Radioanal. Nuclear Chem., v. 253, n. 3, p. 345-350, 2002.

[6] Pereira de Oliveira Junior, O., De Bolle, W., Quétel, C. and Wellum, R., High Accuracy Measurement of Uranium Enrichment $n(^{235}U)/n(^{238}U)$ ratios Evaluating the Uncertainties Associated with Isotope Ratio Measurements Carried Out by by Gas Source and Multi-Collector ICP Mass Spectrometry, ESARDA 25th Annual Meeting, Stockholm, Sweden, 2003.

[7] Pereira de Oliveira Junior, O., De Bolle, W., Alonso, A., Kühn, H, Ponzevera, E., Quétel, C., Richter, S. and Wellum, R., Evaluating the Uncertainties Associated with Isotope Ratio Measurements Carried Out by Different Mass Spectrometry Techniques in Uranium Samples, Symposium on Safeguards and Nuclear Materials Management, ESARDA 27th Annual Meeting, London, England, 2005.

[8] Pereira de Oliveira Junior, O., De Bolle, W., Alonso, A., Kühn, H., Richter, S. and Wellum, R., A New Set of Uranium Isotope Reference Materials for the Improvement of Safeguards in South America, Symposium on Safeguards and Nuclear Materials Management, ESARDA 29th Annual Meeting, Aix en Provence, France, 2007

[9] H. Aigner, R. Binner, E. Kuhn et all, International Target Values 2010 for Measurement Uncertainty in Safeguarding Nuclear Materials, ESARDA Bulletin Nº 31.