

The use of Laser Ablation Sector Field Inductively Coupled Plasma Mass Spectrometry for swipe samples analysis: a viewpoint from Safeguard and Nuclear Forensics

RAFAEL C. MARIN¹, JORGE E. S. SARKIS² and RAFAEL C. B. PESTANA³

¹ Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242, 05508-000 São Paulo, SP
Tel: +55 (11) 3133-9391 - Fax: + 55 (11)3133-9018
marin.rafael.c@gmail.com

²jesarkis@ipen.br

³rcbpestana@gmail.com

ABSTRACT

This work describes the utilization of laser ablation sector field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) for determining uranium isotopic composition in a simulated swipe sample by deposition of U₃O₈ powder with natural enrichment level. This method is useful to measure ²³⁴U/²³⁸U and ²³⁵U/²³⁸U. The measurements were performed on a continuous ablation with low energy density and defocusing, which improved the signal stability, in a cluster of uranium particles. Optimization of measurements was achieved by adjusting the following parameters: RF power, laser beam diameter, defocusing of laser beam, laser energy, laser energy-density, auxiliary gas and sample gas. The ²³⁵U/²³⁸U isotope ratio was 0.00719 ± 0.00020 and its precision was 1.2 % RSD (relative standard deviation). Uncertainties were estimated following the International Organization for Standardization – Guide to the Expression of Uncertainty in Measurement (ISO – GUM), with a confidence level of 95.45% (k = 2.00). The results indicate that the Laser Ablation ICP-MS technique offers a rapid and accurate alternative for the measurement of uranium isotope ratios in uranium particle. The technique has the added advantage of allowing measurements straight on the sample (without further preparation), preserving the testimony which is very important for safeguards and nuclear forensics purposes.

KEYWORDS: nuclear forensics; laser ablation; LA-SF-ICP-MS; uncertainty; uranium; isotope ratio; safeguards

Introduction

Strengthened safeguards procedures arose to prevent clandestine nuclear programmes in States under safeguards agreements. These measures were demonstrated by the Programme 93+2 through a series of field trials. Based on this programme, the use of environmental samples for analyzing uranium enrichment and plutonium separation by means of swipe sampling was established. Swipe samples are taken by wiping various surfaces of nuclear facilities with cotton cloths measuring 10 cm x 10 cm (1; 2; 3). This methodology provides a reliable tool to verify the declarations of the operator, recreate the process history of the material and determine its use (4). Moreover, owing to the increasing number of illicit trafficking of nuclear materials, such procedures are an important element of a new field of science which is responsible to investigate (and determine the source) of seized nuclear materials – nuclear forensics (5; 6).

Globally, only a few laboratories have developed methodologies to analyze swipe samples. These belong to the Network of Analytical Laboratories (NWAL) (4), accredited by the International Atomic Energy Agency (IAEA). The techniques employed by these laboratories include thermal ionization mass spectrometry (TIMS) (7; 8; 9), secondary ion mass spectrometry (SIMS) (10; 11; 12), multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), inductively coupled plasma mass spectrometry (ICP-MS) (13; 14; 15), among others.

The most accurate and most commonly used technique for isotope characterization is TIMS, which is considered the primary technique for isotope ratio measurements by IAEA. However, it is relatively time consuming (several weeks) and requires extensive sample preparation. By contrast, SIMS takes a few days and can identify and perform isotope ratios measurements in individual particles previously deposited on a carbon disk. However, the less abundant isotopes of uranium (^{234}U and ^{236}U) can suffer poly-atomic interferences through the combination of lead with oxygen atoms and carbon atoms from the disk (4).

ICP-MS has been increasingly used to perform isotope ratio measurements (13; 14; 15), owing to its ultra-trace levels capability (fgg^{-1}) (4). It also reaches a precision of down to 0.026% relative standard deviation (RSD) (16; 17). Thus, this technique offers the advantages of ease of operation, multi-elemental analysis (17) and possibility to be coupled to several sample introduction methods, such as Laser Ablation. Recently, laser ablation has been employed in sector field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) for isotopic analysis of single uranium particles down to 10 μm , achieving precision between 0.9 – 5.1% RSD (relative standard deviation) (18) and in one case reaching a precision of 0.1% RSD (19). Moreover, even laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which is quadrupole based, has been used to perform uranium isotopic ratio measurements of single uranium particles previously located by fission track (FT), achieving a precision of 24.2 % RSD (20). These studies indicate that this technique offers a fast and accurate isotopic ratio analysis.

The aim of this work is to determinate uranium isotopic composition of simulated swipe samples using the LA-SF-ICP-MS technique. The analyses were performed based on fundamental metrological concepts following recommendations in the Guide to the Expression of Uncertainty in Measurement (21).

Experimental

Instrumentation

The measurements of isotope ratio were performed using a SF-ICP-MS (Sector Field Inductively Coupled Plasma Mass Spectrometer) ELEMENT1, Thermo Electron Corp., Bremen, Germany. Sensitivity was approximately 1×10^6 cps for 10 ppb of ^{114}In .

The Laser Ablation (LA) measurements were carried out using a Nd:YAG laser at a wavelength of 266 nm, LUV-266X (New Wave Research – Merchantek, Carlsbad - CA, USA).

Materials and Methods

The main operational conditions were established using a Standard Reference Material (SRM) NIST 610 glass supplied by National Institute of Standards and Technology (NIST, USA), which has a concentration of (461.5 ± 1.1) ppm of uranium and was prepared in a rod form, then sliced into wafers.

The method validation and the external correction factor were performed using a Certified Reference Material (CRM) 125-A, a UO_2 pellet certified by NBL (New Brunswick Laboratory, USA), whose the uranium isotopic composition for CRM 125-A is provided in Table 1.

Table 1: Certified values for UO_2 pellet. All data are presented with their expanded uncertainty at 95% confidence level ($k=2$).

Isotope	Atom percent (%)
^{235}U	4.0574 ± 0.0028
^{238}U	95.9049 ± 0.0029
^{234}U	0.0374 ± 0.0003
^{236}U	0.0003 ± 0.0002

The simulated swipe sample was prepared with U_3O_8 natural uranium (NU) particles deposited in an adhesive tape. The sample was then inserted into the laser ablation's chamber and several clusters of uranium material particle were observed. The material was then ablated and carried to the ICP-MS system by an argon flux.

Data evaluation

Mass Discrimination

Mass discrimination is an important effect due to the Coulomb repulsion force suffered by the positively charged ions formed in the plasma. It causes more deflection on light ions than heavy ions. For this reason the isotope ratios must be corrected for each isotope (13; 22). In LA-SF-ICP-MS applications, this effect is much more complex owing to the inter-relationships between laser and target. To minimize these effects a power density of 10^9 Wcm^{-2} (19) and defocused beam (23) was used. The mass fractionation factor was determined by analyzing five independent replicates of UO_2 Certified Reference Material (CRM 125-A) as described by Marin, R.C. et al. (5).

Estimates of Uncertainty

Uncertainty estimates consider all sources of errors in a measurement, i.e. the uncertainty consists of the uncertainty from a standard reference materials certificates, the uncertainty from the repeatability of the measurements and systematic errors. Such estimates allow a better understanding of the results and facilitate comparison with different methodologies. The process of estimating uncertainty adopted in the present study is based on the ISO GUM (21) and has been described in detail in previous studies (5; 24)

Results and discussion

The main operational parameters of the LA-SF-ICP-MS system were optimized using a GLASS standard reference material NIST 610 supplied by National Institute of Standard and Technology (NIST, USA, 1992). The analyses were performed in low resolution mode ($R = 350$) and the main parameters are given in table 2:

Table 2: Optimized parameters for LA-ICP-MS system.

Parameters	Liquid sample	Laser ablation
RF power (W)	1240	1000
Cooling gas (l/min)	16.00	16.00
Auxiliary gas (l/min)	0.91	0.96
Sample gas (l/min)	1.060	1.434
Resolution	LOW	LOW
Run and passes	3 x 1	10 x 2
Mass windows (%)	150 %	5 %
Samples per peak	20	800
Search window (%)	100 %	150 %
Integration window (%)	100 %	100 %
Integration type	Average	Average
Scan type	Escan	Escan
Repetition rate (Hz)	-	10
Laser beam diameter (μm)	-	200
Laser energy (mJ)	-	0.096
Laser energy density (J/cm^2)	-	0.31
Defocusing (mm)	-	1.125

After establishing the initial conditions, the swipe sample prepared for the $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ isotope ratios analyses. The signals of the isotopes measured (^{234}U , ^{235}U and ^{238}U) are very intense in the first few seconds, and then show a decreasing trend which begins to stabilize after seventy seconds. The signal acquisition has already begun by this time and is integrated during the following eighty five seconds.

The isotopic ratios results represent the average of five independent measurements. Thus, they are followed by an inherent error which is represented by their associated uncertainty. It contains all sources of such errors which comprise several components (Table 3) that, when combined, provide the expanded uncertainty. The components of type A are from statistical analysis, whereas the type B components are based on other non-statistical sources.

Table 3 – Uncertainty budget considered to uncertainty estimates. N normal distribution (divisor = 1 for type A uncertainty or divisor = 2 for type B uncertainty inherited from the coverage factor of the CRMs calibration certificate), ci coefficient of sensibility, ui standard uncertainties, vi degree of freedom for each uncertainty quote.

Uncertainty budget							
Name	Type	Dist. Prob.	Divisor	ci	ui 235/238	ui 234/238	vi
CRM measurements	A	N	1	1	0.00009	0.0000049	4
Sample measurement	A	N	1	1	0.000037	0.000001	4
CRM certificate for interest isotope	B	N	1	1	0.000028	0.000003	∞
CRM certificate for ^{238}U	B	N	1	1	0.000015	0.000015	∞

The results obtained for the isotopic ratios $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ (Table 4) gave RSDs of 3.0 % and 1.2 %, respectively. The reproducibility of the isotopic ratio $^{235}\text{U}/^{238}\text{U}$, represented by the standard deviation, is compatible with the percent expanded uncertainty (u %) because they are in the same order of magnitude and thus represent a good estimate of uncertainty. There is good agreement between the precision obtained in this study and that reported by other authors for $^{235}\text{U}/^{238}\text{U}$ isotopic ratio analysis. Ponturier et al. reported RSD of 12.7 % when analyzing natural uranium single particles (20) and 9.6 % RSD when analyzing a sample provided during an interlaboratorial comparison programme (Nusimep-7) (4). Kappel et al. obtained RSD 0.65 % from analysis of glass particles doped with uranium of certified isotopic composition (25) and a range varying from 1.1 % to 3.0 % RSD when analyzing particles from CRM 9073-01-B (26). Lloyd et al. reported precision varying from 0.2 % to 1.8 % from an analysis of depleted uranium in soils (27).

The isotopic ratio corrected by the mass discrimination factor (R_{corr}) for the isotope ^{235}U was 0.00719 ± 0.00020 , which represents a percent atomic abundance of (0.71 ± 0.07) %. A relative difference of -2.1 % was found between this value and the recently recommended atom ratio (0.7257 %) (27). The isotopic ratio $^{234}\text{U}/^{238}\text{U}$ was not concordant with the results of Kappel et al. (25) who also analyzed natural uranium. The relative difference between these values was about 37 % and may be explained by polyatomic interferences caused in minor isotopes at low resolution (18) and by low statistical counts.

Table 4 - Results obtained by LA-SF-ICP-MS analysis of swipe samples for the corrected uranium isotope ratio (R_{corr}), expanded uncertainty (U), percent expanded uncertainty (u %), effective freedom degree (v_{eff}) and coverage factor (k). All data are presented with their expanded uncertainty at 95% confidence level (k=2).

		R_{corr}	U (k=2)	u% (%)	v_{eff}	k (t-Student)
Sample	$^{235}\text{U}/^{238}\text{U}$	0.00719	0.00020	2.8	7	2.51
	$^{234}\text{U}/^{238}\text{U}$	0.000076	0.000031	41	7	2.51

Percent expanded uncertainties were calculated by combining the standard uncertainties (Table 3) and considering a Gaussian distribution (k=2). The result for the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio was in good agreement with the percent expanded uncertainty reported by Kappel et al. which ranged from 1.8 % to 3.9 %. Nevertheless, the u% found for the $^{234}\text{U}/^{238}\text{U}$ isotopic ratios was very high, probably because of uneven signals and mixing effects generated during the simultaneous analysis of several particles.

A t-Student test was performed on the five replicates, because this number is considered low to ensure a Gaussian distribution. This test depends on the effective degree of freedom (v_{eff}) and the distribution probability. The coverage factor calculated by the t-Student distribution was 2.51, indicating that the distribution was slightly different from a normal distribution.

Conclusions

This study demonstrated that the use of LA-SF-ICP-MS to directly analyze swipe samples is reliable, robust, cost effective, and avoids time consuming preparation procedures when compared to wet-based ICP-MS methodologies. The precision and expanded uncertainty estimates were excellent for of the analysis of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio. They make this technique promising from the viewpoint of nuclear safeguards and nuclear forensics; in spite of its destructive analysis characteristics, it consumes only few grams of the sample thereby preserving the evidence. However, it is necessary to evaluate the results to ensure sufficient repetitions increase the degrees of freedom and produce a Gaussian distribution. Moreover, as previously concluded by other authors, the methodology needs to be improved in terms of locating and relocating the particles, thereby increasing the reliability of the technique when analyzing real-life swipe samples.

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