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The use of ICP-MS and LA-ICP-MS techniques for uranium analysis in real-life swipe samples for safeguards purposes

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ABSTRACT

Environmental swipe sampling for safeguards purposes is a powerful tool to detect undeclared materials and activities, and has been used by the International Atomic Energy Agency since 1997. This work describes the utilization of the inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for determining uranium isotopic ratios in a real-life swipe samples collected in a conversion plant at IPEN/CNEN, Brazil. Uncertainties were estimated by following the International Organization for Standardization – Guide to the Expression of Uncertainties in Measurement (ISO GUM), with a confidence level of 95%. The major uncertainties percentage for $n(^{235}U)/n(^{238}U)$ ratio for ICP-MS was 3% and for LA-ICP-MS was 30% The values of uranium isotopic ratios obtained for each technique demonstrate the viability of these analytical techniques as an alternative tool for uranium analysis in swipe samples for safeguards purposes.

KEYWORDS: nuclear safeguards, swipe samples, uranium isotopic ratio, LA-ICP-MS, ICP-MS.

1. INTRODUCTION

Within the nuclear security regime, the safeguards system plays an important tool to verify the absence of illicit nuclear activity in states which assumed to use their nuclear activities only for peaceful purposes. The International Atomic Energy Agency (IAEA) is the responsible for applying the safeguards system to these states[1,2,3].

Environmental samples, including samples collected by wiping a surface at the inspected area, known as swipe samples is one methodology widely employed by the IAEA to verify the nuclear activities in wide-areas (inside and/or vicinity the facilities) in subject to the additional protocol (INFCIRC/540) to safeguards agreements[4,5]. This methodology is complementary to traditional safeguards procedure used to verify the information given by the monitored states[6].

Swipe sampling of nuclear facilities is based on the fact that nuclear installations typically release particulate materials during their activities. For instance the isotopic analysis of the uranium contained in these particles can then be used to reveal important information about the activities performed in the facility[7,8].

However, the analysis of swipe samples requires considerable efforts leading scientists to search for alternative methodologies.

This work aims to compare the use of inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) techniques for uranium analysis of swipe samples for nuclear safeguards purposes.

2. EXPERIMENTAL

Instrumentation

Uranium isotopic ratios $n(^{234}U)/n(^{238}U)$ and $n(^{235}U)/n(^{238}U)$ were performed by ICP-MS (Agilent 7500ce with an octapole reaction system, Hachioji-shi, Tokyo, Japan) using micromist nebulizer and spray chamber operated at 4 °C. The measurements were performed under optimized operating conditions (Table 1). Ultrasound-assisted acid leaching of uranium present in the swipe samples was performed by ultrasound system Thornton T14 (Inpec Eletrônica LTDA, Vinhedo, SP, Brazil).

LA-ICP-MS measurements were performed by ICP-MS, ELAN 6100-DRC (PerkinElmer - Sciex, Waltham - MA, USA) coupled with a Nd:YAG laser at a wavelength of 213 nm using model 213 A/F (New Wave Research, Carlsbad - CA, USA). Argon flux was used to carry the ablated material to the ICP-MS. All measurements were taken under optimized operating conditions (Table 2).

Table 1. Optimized operating condition and data acquisition parameters of ICP-MS analysis.

Instrument and data acquisition settings for the ICP-MS	
Sample and Skimmer cone	Nickel
RF-power (W)	1500
X, Y, Z torch position	Daily
Nebulizer gas flow rate (L/mim)	0.95
Plasma gas flow rate (L/mim)	15
Auxiliary gas flow rate (L/mim)	0.8
Octopole RF (V)	170
Octopole bias voltage (V)	-6
Number of repeats	6
Stabilization time (s)	25
Integration time ^{234}U, ^{235}U and ^{236}U (s)	3
Integration time ^{238}U (s)	0.3
Dwell time (µs)	10

Table 2. Optimized operating condition and data acquisition parameters of LA- ICP-MS analysis.

Parameters	*Laser ablation*
RF Power (W)	1250
Cooling gas (L/min) - Ar	16.00
Auxiliary gas (L/min) - Ar	1.00
Sample gas (L/min) - Ar	0.48
^{234}U dwell time (ms)	75
^{235}U dwell time (ms)	16.7
^{238}U dwell time (ms)	16.7
Replicates	600
Repetition rate (Hz)	10
Laser beam diameter (μm)	200
Laser energy (mJ)	0.096
Ar flux (L/min)	0.46

Materials and Methods

Nitric acid, Merck® and Milli-Q®-purified water (Millipore, France), with resistivity 18.2 MΩ.cm at 25 °C, were used in the assays. All containment vessels were cleaned with 1.45 mol.kg^{-1} nitric acid and Milli-Q water before use.

The uncertainties were calculated following the ISO GUM[9], taking into account all the components that associated with the result which characterizes the dispersion of real values. The mass discrimination correction was applied, following the equations used by PESTANA, 2013[4], analyzing a Certified Reference Material (CRM) from NIST, NBS U200 (former National Bureau of Standards) for ICP-MS samples and CRM from NBL (New Brunswick Laboratory) 125 A for LA-ICP-MS samples.

Swipe sampling area:

The Nuclear and Energy Research Institute (IPEN/CNEN), São Paulo, Brazil, operates a MTR research reactor, IEA-R1, which uses uranium enriched up to 20% of ^{235}U as nuclear fuel. This material is produced at the Nuclear Fuel Center department (CCN, IPEN/CNEN)[4]. The samples were collected in a conversion plant which converts UF_6 into an intermediate compound, UF_4, necessary to produce the U_3Si_2-Al alloy used as a nuclear fuel in IEA-R1.

The samples were collected in replicate at the same point and each sample was analysed according Table 3.

Table 3: Description of the swipe sample collection points around and within the conversion plant and the techniques used.

Sample	Technique	Point description
1	ICP-MS	Facility entrance [A]
2	LA-ICP-MS	Facility entrance [A]
3	ICP-MS	Radiation meter door [B]
4	LA-ICP-MS	Radiation meter door [B]
5	ICP-MS	Exhaust pipe UF_4 recovery [B]
6	LA-ICP-MS	Exhaust pipe UF_4 recovery [B]

A – Outside the facility
B – Within the facility

Ultrasound-assisted acid leaching (UAL)

The use of UAL for recovery uranium present in the swipe samples was proposed by PESTANA et al, 2013[4]. The samples were placed into clean polystyrene centrifuge tube containing 20g of 0.29 mol.kg-1 HNO3 and kept in ultra-sound bath for 15 minutes.

The samples were then removed from polystyrene tube and the remaining solution was centrifuged at 3,000 rpm for 3 minutes. The supernatant was transferred to a clean polystyrene centrifuge tube and introduced directly in the ICP-MS for uranium isotopic ratio analysis.

Laser Ablation (LA)

Swipe samples were kept in an individual sealed plastic bag until analysis, at which time they were directly inserted into the Laser Ablation chamber without further preparation.

The use of LA for swipe samples was following the method proposed by MARIN et al, 2013[10]: before acquiring the data, an ablation of 60 s was performed to stabilize the laser signal. The measurements were performed on a continuous ablation with low energy density and defocusing.

3. RESULTS AND DISCUSSION

Mass discrimination factors (Fmd) were determined for both techniques and are shown in Table 4. These values were used to correct the measurement of the isotopic ratios in the samples.

Table 4: The mass discrimination factors (Fmd) values obtained by ICP-MS and LA-ICP-MS

	CRM	$n(^{234}U)/n(^{238}U) \pm U^*$	$n(^{235}U)/n(^{238}U) \pm U^*$
ICP-MS	NBS U200	0.991 ± 0.033	0.9925 ± 0.0077
LA-ICP-MS	NBL 125 A	1.146 ± 0.012	1.1457 ± 0.0016

*U= expanded uncertainty with confidence level of 95%.

As show in the Table 4, the relative error for Fmd in n(^{235}U)/n(^{238}U) ratio was 0.8% (ICP-MS) and 14.6% (LA-CP-MS). The high value of Fmd obtained by LA-ICP-MS is related to the intrinsic instability of the laser ablation, thus, as expected, the Fmd is a relevant component of the final result of isotopic ratio and its expanded uncertainty (Table 6).

The corrected isotopic ratios obtained for the swipe samples are shown in Table 5 (ICP-MS) and Table 6 (LA-ICP-MS).

Table 5: Isotopic ratios values for the samples submitted for UAL method and its expanded uncertainty.

Sample	n(^{234}U)/n(^{238}U)	±U*	n(^{235}U)/n(^{238}U)	±U*
1	0.0003	0.0002	0.040	0.004
3	0.0015	0.0003	0.166	0.005
5	0.0016	0.0003	0.185	0.005

*U= expanded uncertainty with confidence level of 95%.

Table 6: Isotopic ratios values and expanded uncertainties obtained by LA-ICP-MS of the swipe samples

Sample	n(^{234}U)/n(^{238}U)	±U*	n(^{235}U)/n(^{238}U)	±U*
2	0.0006	0.0001	0.023	0.007
4	0.0016	0.0004	0.159	0.024
6	0.0017	0.0003	0.195	0.032

*U= expanded uncertainty with confidence level of 95%.

Table 7 presents the results obtained by the swipe samples expressed in atoms percentage.

Table 7: Atomic percentage values relative to the ^{235}U isotope for all samples used in this study and its uncertainties.

Sample	Technique	Atomic % ^{235}U	± U*	± U %**
1	ICP-MS	3.89	0.07	1.8
2	LA-ICP-MS	2.3	0.7	30.4
3	ICP-MS	14.2	0.3	2.1
4	LA-ICP-MS	13.7	2.1	15.3
5	ICP-MS	15.6	0.3	1.9
6	LA-ICP-MS	16.1	2.7	16.8

*U= expanded uncertainty with confidence level of 95%.
**U% = percent of expanded uncertainty

As it can be observed in Table 7, for higher enrichment levels the results are in good agreement within the uncertainty of both techniques. For the low enrichment sample (1 and 2) the results are in the same order of magnitude, but presented considerable differences (circa of 42 %). However, it is important to notice that this measurements were performed using different samples collected at the same point. In the case of samples 1 and 2 the sampling were performed close to the entrance door of the facility, therefore, can suffer more influence of the uranium naturally present in the environment.

Figure 1 shows atomic percentage relative to the ^{235}U isotope.

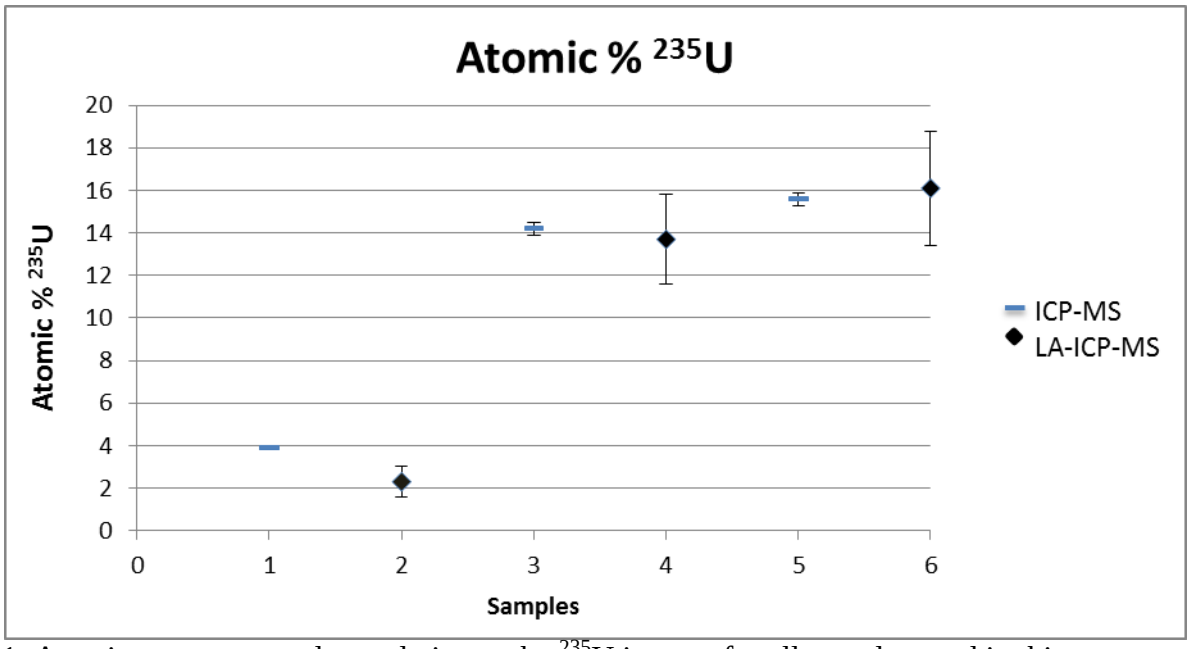

Figure 1: Atomic percentage values relative to the ^{235}U isotope for all samples used in this study and its expanded uncertainties.

It is important to note that natural uranium is also manipulated in the facility, which may explain the low enrichment values (below 20 % of ^{235}U) found in all the analyses

4. CONCLUSIONS

Nowadays, the swipe samples analysis plays an important role in the nuclear safeguards. Thus, many environmental samples are collected, requiring great efforts from the safeguards laboratories in developing new methodologies for their analysis.

In this manner, as it was demonstrated, the use of ICP-MS and LA-ICP-MS provided similar results, within the estimate of its uncertainties, demonstrating the viability of these techniques for uranium analyses in real-life swipe samples.

Results obtained by both techniques are in good agreement, the minor differences between the methods could be due to the heterogeneity of the samples, the amount of existing uranium in each swipe sample, the presence of natural uranium (also manipulated within the facility) and the inherent unevenness of laser ablation.

The UAL method is simple, reliable, fast and efficient. The reduced time, ~15 min, necessary to extract uranium in swipe sample is a great advantage, especially when a large number of samples need to be analyzed. The method significantly decreases the number preparation steps, thereby reducing the risk of contamination when compared to traditional bulk analysis (total digestion and chemical separation).

In comparison with wet-based methodologies, uranium isotope ratios bulk analysis from real-life swipe samples by LA-ICP-MS avoids chemical preparation procedures and preserve the major part of the sample. Therefore, due the heterogeneity of the sample as well as the known unevenness of the laser ablation the results present high levels of uncertainty requiring more development to be useful for safeguards purposes.

Calculation of the uncertainty of measurement is extremely important to establish the degree of trustworthiness of the obtained data. The major uncertainty, for n(^{235}U)/n(^{238}U) ratio and for the samples collected inside the facility, obtained in this work by ICP-MS was 3% and by LA-ICP-MS was 30%.

Therefore, if is necessary to bring more reliability and precision to the uranium enrichment level determination for nuclear safeguards purposes the swipe sample analysis has to be considered alternative techniques could include MC-ICP-MS, SF-ICP-MS, SIMS or TIMS.

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