

The use of LA-SF-ICP-MS for nuclear forensics purposes: uranium isotope ratio analysis

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Abstract This work describes the utilization of the laser ablation sector field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) technique for the determination of uranium isotopic composition in a highly enriched uranium sample. The measurements were performed on a continuous ablation with low energy density and defocusing, which demonstrated to be the optimum to reach the best signal stability. The measurements were improved 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 $^{235}\text{U}/^{238}\text{U}$ isotope ratio with its respective uncertainty was 16.36 ± 0.15 and its precision was 1.12 % relative standard deviation. The uncertainties were estimated following the ISO GUM, with a confidence level of 95.45 % ($k = 2.00$). When compared the isotope abundances to the Round Robin Exercise Number 3's average results a difference of 0.46 % has been found and when compared to supplier's value, the difference was 0.41 %. The results presented by the measurements revealed that the LA-ICP-MS technique offers a rapid and accurate alternative to measure uranium isotope ratios without any sample

preparation, since it allows carrying out the measurements straight on the sample. Moreover, it preserves the testimony—very important for safeguards and nuclear forensics purposes.

Keywords Nuclear forensics · Laser ablation · LA-SF-ICP-MS · Uncertainty · Uranium · Isotope ratio

Introduction

The beginning of the 1990s was characterized by several incidents involving illicit trafficking of nuclear material. As a result, a new field of knowledge defined as nuclear forensics was developed, being responsible to investigate the smuggling and the illicit traffic of radioactive and nuclear materials. During a nuclear forensics investigation several questions have to be answered. Among them: the nature of the material, the mode of production, the intended use, the origin, the nuclear facility, the last legal owner and the trafficking route [1, 2]. In this context, uranium isotope ratio plays a key role.

The technique which provides better accuracy and is most often used to isotope characterization is thermal ionization mass spectrometry (TIMS), which is considered the primary technique for isotope ratio measurements by the International Atomic Energy Agency. However it is a relatively time consuming technique and requires extensive sample preparation [2–5]. There are also other techniques employed to perform uranium isotope ratio measurements, such as: high resolution gamma-ray spectrometry (HRGS), gas source mass spectrometry, glow discharge mass spectrometry, secondary ion mass spectrometry, among others [6] with advantages and drawbacks.

During the last years the inductively coupled plasma mass spectrometry (ICP-MS) have been increasingly used

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to perform isotope ratio measurements [7–9], being capable to measure isotope ratios at ultra-trace levels, down to fgg^{-1} [10] and reaching precision down to 0.026 % relative standard deviation (RSD) [8, 9]. When compared to TIMS, the ICP-MS technique offers the advantage of ease operation, multi-elemental analysis [9] and possibility to be coupled to several sample introduction methods, such as laser ablation (LA) [3, 7]. Former studies had employed LA-sector field ICP-MS (SF-ICP-MS) for isotopic analysis of single uranium particles down to 10 μm and achieved precision between 0.9 and 5.1 % RSD [3, 7], reaching precision down to 0.1 % RSD [6]. Those studies have concluded that this technique offers a fast and accurate isotopic ratio analysis. This technique has been growing substantially among the analytical techniques due to its good accuracy followed by possibility of direct analysis without sample preparation, relying to sample preservation and with the use of low amount of sample.

The aim of this work is to determinate uranium isotopic composition for nuclear forensic purposes using the LA-SF-ICP-MS technique. The analyses were performed based on fundamental metrological concepts following the Guide to the Expression of Uncertainty in Measurement recommendations [11].

Experimental

Instrumentation

The measurements of isotope ratio were performed using a SF-ICP-MS ELEMENT1, Thermo Electron Corp., Bremen, Germany.

The 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). The ablated material was transported by argon as a carrier gas into the plasma.

Standard and samples

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).

The method validation was performed using a CRM (certified reference material) 125-A, a UO_2 pellet certified by New Brunswick Laboratory, USA. A single production batch of pellets prepared by Westinghouse Commercial Nuclear Fuels Division, Columbia, South Carolina. Its isotopic composition is presented in Table 1.

The sample analyzed was highly enriched uranium (HEU) rod used during the Round Robin Exercise Number

Table 1 Certified values for UO_2 pellet

Isotope	At. %
^{235}U	4.0574 ± 0.0028
^{238}U	95.9049 ± 0.0029
^{234}U	0.0374 ± 0.0003
^{236}U	0.0003 ± 0.0002

All data are presented with their expanded uncertainty at 95 % confidence level ($k = 2$)

3 (RR3) organized by the Nuclear Smuggling International Technical Working Group organized by the Nuclear Forensics International Technical Working Group (ITWG) and supplied by the US Department of Energy.

Data evaluation

Mass discrimination

An important effect to be considerate during the uranium isotopic ratio measurements is the mass discrimination (CF), occurring when the positively charged ions formed in the plasma suffer action of the Coulomb repulsion force, resulting in a loss of transmission through the ion optical lens. It occurs because the light ions are more deflected than the heavy ones. For this reason, the isotope ratios must be corrected for each isotope [4, 12, 13]. The CF effects for LA-SF-ICP-MS is the result of a complex series of inter-relationships among the laser-target interactions, transport efficiencies and the behavior of the amount ablated in the argon plasma. The shorter the wavelengths, the less sensitive are the CF effects. To minimize those effects could be performed a LA with a power density of 10^9 W cm^{-2} [6] and defocused beam [3].

In this paper the mass fractionation factor was determined analyzing a UO_2 CRM 125-A. It depends on the mass differences between the isotopes; therefore there is a correction factor for each isotope. For this purpose five independent replicates analyses were performed and the results were corrected by the mass fractionation factor (CF) using the power law, which is more appropriate for ICP-MS:

$$\text{CF} = \frac{(f_{\text{md}} - 1)}{\Delta_m} \quad (1)$$

where CF is the mass discrimination, f_{md} is the mass discrimination factor and Δ_m is the difference of nominal masses.

With:

$$f_{\text{md}} = \frac{R_{\text{certified}}}{R_{\text{measured}}} \quad (2)$$

where f_{md} is the mass discrimination factor, $R_{\text{certified}}$ is the CRMs certified isotope ratio and R_{measured} is the CRMs measured isotope ratio.

Once calculated the CF, the isotope ratio is corrected by the expression (3):

$$R_{\text{corr}} = R_{\text{m}}(1 + \text{CF})^{\Delta_m} \quad (3)$$

where R_{corr} is the isotope ratio measured corrected by the CF, R_{meas} is the isotope ratio measured, CF is the mass discrimination and Δ_m is the difference of nominal masses.

Estimative of uncertainty

Every measurement is subject to some degree of variability. This variability can come from different sources as from the measuring instrument, from the item being measured, from the environment etc. and represents the analytical uncertainty of the measurement. The uncertainty estimative considers all components of the analytical procedure.

Therefore, the estimation of the uncertainty associated with an analytical measurement allows better understanding of the measurement process, being an essential part of it—as facilitates the inter-comparison of analytical results obtained from different laboratories and methodologies.

The estimation of the uncertainty is commonly based on ISO GUM [11], considering all dominant components of the measurement and the combined uncertainty (u_c) (4) allowing in-depth understanding of the measurement process.

$$u_c = \sqrt{\sum_{i=1}^n u(x_i)^2} \quad (4)$$

where u_c is the combined uncertainty, $u(x_i)$ is the standard uncertainty.

The standard uncertainty $u(x_i)$ for each input is evaluated by the following criterion: type A, which considers the standard deviation of the mean of a series of observations; type B, which considers all available information such as external sources, calibration certificates, manufacturer's uncertainty and judgment based on experience [11, 14].

The final result of a measurement is expressed to yield a coverage factor of a chosen level of confidence, which is determined from the t -Student distribution and the calculated effective degrees of freedom (5).

$$v_{\text{eff}} = \frac{u_c^4}{\sum_{i=1}^n \frac{u_i^4}{v_i}} \quad (5)$$

where v_{eff} is the effective degrees of freedom, u_c is the combined uncertainty, u_i is the uncertainty quotes, v_i is the degrees of freedom for each uncertainty quote.

Table 2 Optimized parameters for LA-SF-ICP-MS system

Parameters	LA
RF power (W)	1000
Cooling gas (l/min)	16.00
Auxiliary gas (l/min)	0.96
Sample gas (l/min)	1.434
Resolution	350
Run and passes	8 × 3
Mass windows (%)	5
Samples per peak	800
Search window (%)	100
Integration window (%)	100
Integration type	Average
Scan type	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)	2.692

The level of confidence of 95.45 % corresponds to a coverage factor of $k = 2.00$ and 99.73 % to $k = 3.00$ [14]. Therefore, the expanded uncertainty (U) (6) is calculated by the following equation:

$$U = u_c k \quad (6)$$

where U is the expanded uncertainty, u_c is the combined uncertainty, k is the coverage factor.

The result of the measurement is expressed as the average of the measurements followed by its expanded uncertainty: $y_{\text{avg}} \pm U$.

Results and discussions

Initially, the main operational parameters of the LA-SF-ICP-MS system were optimized using a GLASS SRM NIST 610 supplied by NIST (USA, 1992) as described by Varga [7] and Marin and Sarkis [3]. The analysis were performed in low resolution mode ($R = 350$) and the main parameters are presented in Table 2:

These conditions were used to measure uranium isotope ratios in the CRM 125-A, in five independent replicates. The results are presented in Fig. 1.

As it can be observed the $^{235}\text{U}/^{238}\text{U}$ isotope ratios presented the best precision, about 1.17 % RSD. However, for the less abundant isotopes the stability worsened, which could be explained for the low statistical counts of the minor isotopes (^{234}U and ^{236}U).

Based on these adjustments, uranium isotope ratios were measured in a HEU sample. In order to obtain comparable

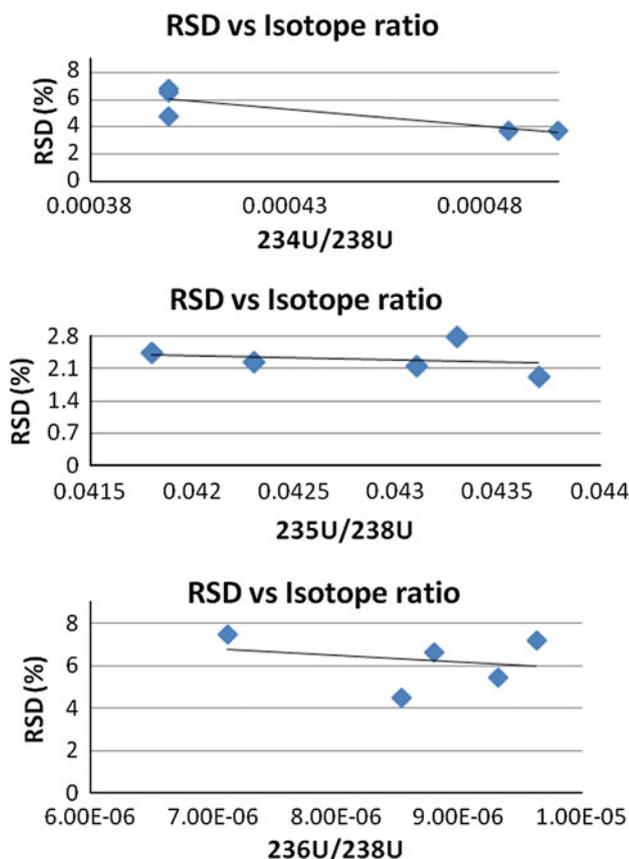


Fig. 1 Isotope ratio stability RSD versus isotope ratio for the standard UO₂ pellet

data were considered the following uncertainties budgets to estimate the expanded uncertainty (*U*): the mean standard deviation of the measurements (type A uncertainty) and the isotope abundances reported in the calibration certificate of CRM 125-A (type B uncertainty) as shown in Table 3. The uncertainty inherited from the CRMs calibration certificate has normal distribution and its divisor is the coverage factor (*k*) which was reported in the certificate.

The uncertainty due to the sample measurement (i.e. the repeatability of the measurement) was the major contributor for the ²³⁵U/²³⁸U uncertainty. It is due to the

Table 4 Combined uncertainty (*u_c*), expanded uncertainty (*U*), effective degree of freedom (*v_{eff}*) and coverage factor (*k*) for uranium isotope measurements

Isotope ratios	<i>u_c</i>	<i>U</i>	<i>v_{eff}</i>	<i>k</i>
²³⁵ U/ ²³⁸ U	0.075341839	0.15	5	2.57
²³⁴ U/ ²³⁸ U	0.00233142	0.005	13	2.16
²³⁶ U/ ²³⁸ U	0.004078659	0.008	7	2.39

All data are presented with their expanded uncertainty at 95 % confidence level (*k* = 2)

variability on the measurement. For the other isotopes, besides the low statistical counts, the uncertainty was low due to the great repeatability.

The Table 4 presents the expanded uncertainty (*U*); the effective level of freedom and the coverage factor were calculated based on the data shown in Table 3.

According to Table 4, it was noticed that the effective coverage factor, determined by the *t*-Student distribution, for the ²³⁵U/²³⁸U was *k* = 2.57, while for the ²³⁴U/²³⁸U *k* was 2.16 and for ²³⁶U/²³⁸U *k* was 2.39. It was due to the mean standard deviation of the measurements of sample was the major contribution for the combined uncertainty (*u_c*).

The measured values for the uranium isotope ratios, the corrected values calculated by the expression (3) and the mass fractionation factor (*f_{md}*), with their respective uncertainties, were summarized in the Table 5. It could be noticed that the CF factor varied from 0.32 ± 0.11 to 0.9790 ± 0.0016. The CF factor is supposed to be as close to the unity as possible, which was achieved to the ²³⁵U/²³⁸U measurement. However, for the ²³⁶U/²³⁸U the *f_{md}* was 0.32 and for the ²³⁴U/²³⁸U the *f_{md}* was 0.7680 which were very different from the unity. It could be due to the wrong background correction combined to the low abundance of these minor isotopes.

The major contribution for the overall uncertainty is due to the precision of the measurement, which is affected by the LA unevenness that disturbs the plasma. It can be noticed by the internal precision of the measurement, which varied from 2.19–5.99 % RSD for major isotopes,

Table 3 Uncertainty budget for uranium isotope ratio analysis

Uncertainty budget								
Name	Type	Probability distribution	Divisor	<i>c_i</i>	<i>u_i</i> (235/238)	<i>u_i</i> (234/238)	<i>u_i</i> (236/238)	<i>v_i</i>
CRM 125-A measurement	A	N	1	1	0.0000667	0	0.0000004	5
Sample measurement	A	N	1	1	0.0753	0.0018	0.0038	5
CRM certificate for interest isotope	B	N	2	1	0.0028	0.0003	0.0002	∞
CRM certificate for ²³⁸ U	B	N	2	1	0.0029	0.0029	0.0029	∞

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), *c_i* coefficient of sensibility, *u_i* standard uncertainties, *v_i* degree of freedom for each uncertainty quote

while the external one was 1.12 % RSD. However, the precision achieved in this study is comparable to former studies that have achieved RSD from 0.9 to 5.1 % [7]. It showed that the variability (type A uncertainty component) of the measurement is the most significant component of the uncertainty. Nevertheless, the expanded uncertainty (U), for the major isotope ratio ($^{235}\text{U}/^{238}\text{U}$), presented in the Table 4 ($U = 0.15$) is also comparable to the expanded uncertainty achieved by Varga [7] ($U = 0.20$) for the same isotope ratio and with coverage factor $k = 2.00$.

Based on the results of the isotope ratios shown in Table 5, the isotope abundance can be calculated by the following expression:

$$F_{235} = 100x \frac{\frac{^{235}\text{U}}{^{238}\text{U}}}{1 + \frac{^{234}\text{U}}{^{238}\text{U}} + \frac{^{235}\text{U}}{^{238}\text{U}} + \frac{^{236}\text{U}}{^{238}\text{U}}} \quad (7)$$

where F_{235} is the percent atom abundance for ^{235}U isotope, $^{234}\text{U}/^{238}\text{U}$ is the isotope ratio between $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ is the isotope ratio between $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ is the isotope ratio between $^{236}\text{U}/^{238}\text{U}$.

The ^{235}U percent atom abundance achieved by the expression (7) was $(93.31 \pm 1.02)\%$ for the corrected values and $(93.0 \pm 1.0)\%$ for non corrected ones, showing that the correction applied by the CF factor is paramount for reliable results, since the supplier value, shown in Table 6, is 92.929 for $^{235}\text{U}/^{238}\text{U}$ isotope ratio.

Table 5 Corrected isotope ratio values for uranium isotope ratio of the HEU sample and the CF factor

	Measured	Corrected	CF factor (f_{md})
$^{234}\text{U}/^{238}\text{U}$	0.182 ± 0.005	0.144 ± 0.005	0.7680 ± 0.0031
$^{235}\text{U}/^{238}\text{U}$	16.71 ± 0.15	16.36 ± 0.15	0.9790 ± 0.0016
$^{236}\text{U}/^{238}\text{U}$	0.0703 ± 0.0014	0.031 ± 0.008	0.32 ± 0.11

All data are presented with their expanded uncertainty at 95 % confidence level ($k = 2$)

Table 6 RR3 uranium isotopic analysis results for sample A (in at.%) [15]

Laboratory (methods)	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
Columbia (TIMS)	0.0006 ± 0.0003	1.0048 ± 0.0027	92.9769 ± 0.0124	0.3867 ± 0.0021	5.6310 ± 0.0076
Danube (TIMS)	NR	1.00 ± 0.002	92.97 ± 0.015	0.387 ± 0.001	5.639 ± 0.014
Murray-Darling (ICP-MS)	NR	1.08 ± 0.01	93 ± 0.9	0.45 ± 0.005	5.49 ± 0.05
Nile (MC-ICP-MS)	0.00004 ± 0.00001	1.0035 ± 0.0011	92.966 ± 0.004	0.3884 ± 0.0006	5.6419 ± 0.0026
Orinoco (HRGS)	NR	1.1 ± 0.09	92.8 ± 1	NR	6.1 ± 0.5
Tigris (ICP-MS)	NR	0.965 ± 0.009	92.5 ± 0.69	0.346 ± 0.002	6.1 ± 0.48
Ural (MC-ICP-MS)	$(32.9 \pm 4.4) \times 10^{-6}$	1.0037 ± 0.0004	92.9832 ± 0.0085	0.38597 ± 0.00056	5.6271 ± 0.0061
Yangtze (HRGS)	NR	0.89 ± 0.52	92.75 ± 2.64	NR	6.35 ± 0.23
Yukon (ICP-MS)	NR	1.006 ± 0.013	92.96 ± 0.07	0.3867 ± 0.0043	5.64 ± 0.05
Supplier	NR	0.999	92.929	0.386	5.686

All data are presented with their expanded uncertainty at 95 % confidence level ($k = 2$)

Table 7 Percent atoms abundance ($A\%$) for uranium isotope ratios

	Corrected	Supplier	Relative deviation (%)
F_{234}	0.818 ± 0.027	0.999	-18.11
F_{235}	93.31 ± 1.02	92.929	0.41
F_{236}	0.175 ± 0.047	0.386	-54.66
F_{238}	5.702 ± 0.067	5.686	0.28

All data are presented with their expanded uncertainty at 95 % confidence level ($k = 2$)

Table 8 Comparison between the enrichments achieved in this work and the enrichments achieved in the RR3 exercise [15]

	F_{235} relative deviation (%)
Murray-Darling (ICP-MS)	0.33
Orinoco (HRGS)	0.55
Tigris (ICP-MS)	0.88
Yangtze (HRGS)	0.60
Supplier	0.41

If compared the RR3s average results for $^{235}\text{U}/^{238}\text{U}$ with the supplier's values, shown in the Table 6, was achieved relative deviation of -0.053% . When compared to the corrected isotope abundance (Table 7) obtained by this work to the average of RR3s results [15], was achieved a difference of 0.46% . Comparing the results of Table 7 to the supplier's rod value, there is a difference of only 0.41% for the corrected values.

In Table 7 can be noticed a peculiarity found in the optimization procedure (Fig. 1), that is the technique's instability for low abundant isotopes, which led the difference between the supplier's and the measured value to a higher level than the most abundant isotopes. The differences of -18.11 and -54.66% for the F_{234} and F_{236} , respectively, were due to the CF factor for the ^{234}U and ^{236}U isotopes, which were different to the unity.

A comparison between the isotope abundance achieved at the present study and those reported by ITWGs RR3 exercise [15], presented in Table 8, shows that the relative deviation reached in this work was less than 0.9 % from the other participants and most important: less than 0.5 % from the supplier's result. The results achieved corroborate with several authors [3, 6–8] which stated that the LA-SF-ICP-MS is a promising and robust technique for performing isotope ratios analysis with precision, accuracy, low time consuming and without sample preparation.

Conclusion

In this work, it was found a great accordance with the value of the rod's supplier after resort the soft ablation and defocusing beam strategy [3, 5, 7], which minimizes the mass fractionation effects and brings the necessary precision and accuracy to distinguish the different categories of origin of the nuclear materials. Thus, when observed the advantages of the method proposed, such as direct and fast sample analysis, low sample amount, sample preservation, non-contamination of the sample and multi-elemental analysis, is possible to state that this technique shows itself very robust. The low uncertainty found when applied the correction factor together with the replicated sample analysis shows the strength of the present technique, since it mitigates the effects of its instability. This disadvantage caused to LA characteristics was improved by making replicated measurements. Another relevant issue discussed in this work was the uncertainties estimative suggested by the ISO GUM manual, which improves the uncertainty, bringing more metrological quality to the measurement.

Despite the large corrections applied to the minor isotopes (^{234}U and ^{236}U), the overall isotope ratio measurements by LA-SF-ICP-MS shows a great tool to perform nuclear forensics studies, since this work achieved relative deviation to 0.41 % from those reported by the ITWGs RR3 inter-laboratory comparison, the technique's internal precision obtained for the isotopes were between 1.91 and 5.99 % RSD and the isotope ratio for $^{235}\text{U}/^{238}\text{U}$ was 16.36 ± 0.15 , representing a percent atom abundance of $(93.31 \pm 1.02)\%$. Adopting the recommendations of ISO GUM for the estimative of uncertainties allowed better understanding of the measurement processes and had generated most comparable data. Therefore, the use of LA-SF-ICP-MS to perform uranium isotope ratios proposes can be a promising and robust method for nuclear forensic,

since was found a small difference between the results achieved in the present study and those reported by the supplier of the RR3 exercise.

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