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ISOTOPE RATIO MEASUREMENTS OF URANIUM BY LA-HR-ICP-MS

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ABSTRACT

This work describes the utilization of Laser Ablation High Resolution Inductively Mass Spectrometry (LA-HR-ICP-MS) technique for the determination of uranium isotope composition in a UO_2 pellet (CRM -125A) supplied and certified by the New Brunswick Laboratory (NBL). To carry out the adjustments of the parameters was used a glass standard NIST 610, supplied and certified by National Institute of Standards and Technology (NIST). The precision of 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 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.
Isotope ratios, $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ were measured, reaching relative standard deviations (RSD) from 1.55% to 7.60%. The parameters which caused the greatest impact in order to improve the signal stability were RF power, defocusing and laser beam diameter. The results presented by the measurements revealed that the Laser ablation ICP-MS technique offers a rapid and accurate way to perform uranium isotope ratios without any sample preparation, since it allows carrying out the measurements straight on the sample, besides to preserve the testimony that is very important for safeguards and nuclear forensics purposes.

1. INTRODUCTION

The measurements of uranium isotope ratios are extremely important and have been studied for several fields such as geosciences, environmental science, nuclear science, nuclear forensics and safeguards. From the viewpoint of nuclear forensics and safeguards, the uranium isotope ratio measurement is crucial to detect illegal or undeclared activities [1].

During the last years several techniques have been used for this purpose, such as: Thermal Ionization Mass Spectrometry (TIMS) [6, 7], Inductively Coupled Plasma Mass Spectrometry (ICPMS) [6, 8], High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) [6], Glow Discharge Mass Spectrometry (GDMS), Secondary Ion Mass Spectrometry (SIMS), among others [2]. The technique which provides better accuracy and it is most often used to isotope ratio measurements is TIMS, which is considered the primary technique for isotope ratio measurements by IAEA (International Atomic Energy Agency).

In the last decades there has been a significant increase in the use of ICP-MS technique for the measurement of radionuclide due to its accuracy, precision and excellent sensitivity, reaching the order of fg/g [3]. All of these characteristics, coupled with the analytical speed, multi-element analysis and the possibility of connecting several methods of sample introduction, such as the laser ablation (LA) technique, makes ICP-MS widely used. So, the use of LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) as direct method of introduction of sample has been consolidated in the analysis of solids due to its characteristics of direct analysis of samples without the need of digestion, without generating waste; ability to micro analysis; and low amount of sample needed for analysis, preserving the testimony [2]. Its major limitation with respect to the isotope ratio measurements is the instability caused by the plasma and the ablation process itself, but the technological innovations of the last decade took their limit of detection at ng/g or μg/g, depending on the type of the sample, which corresponds to fg - pg if the value is presented in absolute terms [5]. Besides the easiness of the sample introduction there is the advantage of preserving the sample or testimony that represents a great advantage, when it comes to forensics nuclear.

The figure 1 shows a schematic of LA-HR-ICP-MS system:

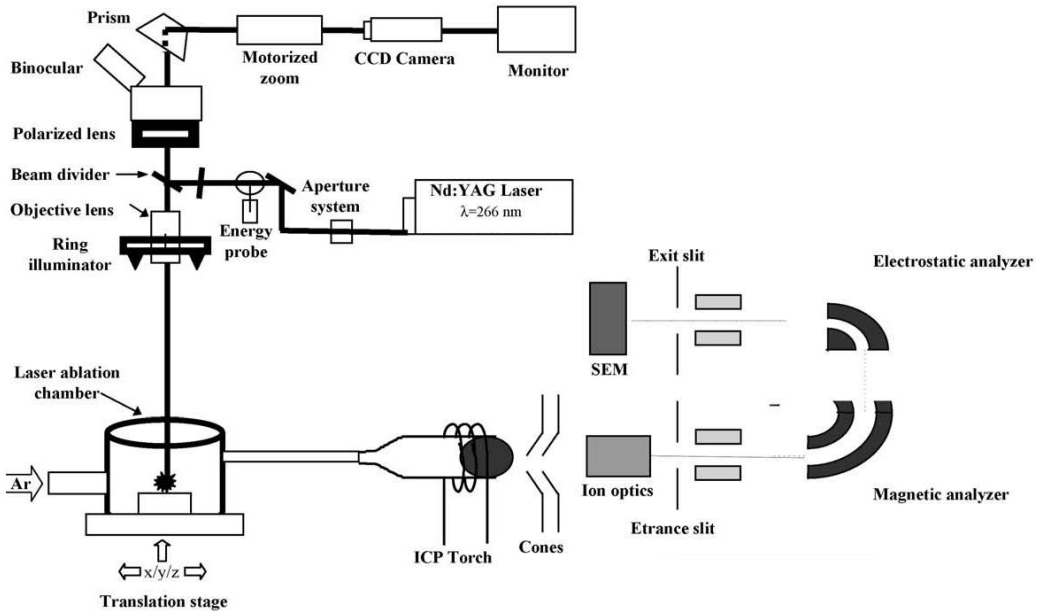


Figure 1: LA-ICP-MS system [1].

The aim of this study was to perform measurements of isotope ratios of uranium pellets supplied by NBL (New Brunswick Laboratory). In it were discussed the adjustment parameters of Laser Ablation (LA) system, ICP-MS (Inductively Coupled Plasma Mass

Spectrometry) and the adequacy of the results with the nominal isotope ratio of the pellet in question.

2. EXPERIMENTAL

2.1. Instrumentation

The measurements of isotope ratio were performed using a HR-ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometer) equipped with a single electron multiplier (ELEMENT1, Thermo Electron Corp., Bremen, Germany). The tune adjustments of the ICP-MS were performed in low resolution mode using liquid sample introduction. The optimization was carried out with respect to maximum ^{115}In sensitivity, which was about $1x10^6$ cps. The optimized parameters were summarized in table 1.

The Laser Ablation (LA) measurements were carried out using an LUV-266X laser ablation system (New Wave Research – Merchantek, Carlsbad - CA, USA). Laser ablation was performed with a Nd:YAG laser at a wavelength of 266 nm. The ablated material was transported by argon as a carrier gas into the plasma. Optimization was performed using a NIST 610 glass reference material (NIST, Gaithersburg, USA) with respect to maximum ^{238}U intensity. Laser ablation parameters used for the optimization: pre-ablation time: 60s, continuous spot, repetition rate: 10 Hz, laser beam diameter: 200 μm, laser energy: 40% (0.096 mJ), laser energy density (0.31J/cm^2) and z axis position with 1.125 mm above the sample surface. Sensitivity was approximately 1.34×10^6 cps. The optimized parameters were shown in table 1.

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

Table 1: Optimized parameters for LA-ICP-MS system.

2.2. Standard and samples

The primary adjustments of the Laser Ablation system were performed using the Standard Reference Material (SRM) NIST 610, trace elements in a glass matrix, supplied and certified by National Institute of Standard & Technology (NIST). The certified U concentration in the SRM was (461.5 ± 1.1) μg/g. It was prepared in a rod form and then sliced into wafers. Its support matrix is composed of 72% SiO_2, 12% CaO, 14% Na_2O and 2% Al_2O_3.

In order to simulate a real sample, a certified reference material, CRM 125-A (UO_2 pellet), certificated by NBL (New Brunswick Laboratory) was used. This is a single production batch of pellets prepared by Westinghouse Commercial Nuclear Fuels Division (CNFD), Columbia, South Carolina. Its percent atom abundance was shown at the table 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

Table 2: Certified values for UO_2 pellet.

2.3. Results and Discussions

In order to determine the better conditions for signal stability and sensitivity several ablation trials were performed changing the main laser parameters such as: RF power, laser beam diameter and z axis position (defocusing) using the SRM NIST 610 as reference material. Those adjustments were performed with a pre-ablation time of 1 min. and an acquisition time of 1 min. in a continuous spot.

The first parameter to be evaluated was the RF power. The results are presented in the figure 2.

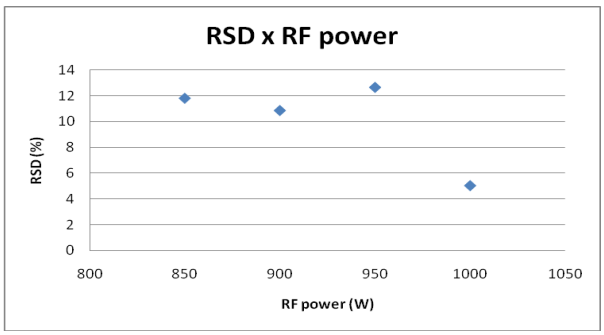


Figure 2: Adjustment data for RF power.

Observing the figure 2 was noticed that the better precision occurs at 1000 W, due its low RSD (Relative Standard Deviation). Therefore, the first parameter established was the RF power.

In order to verify the great signal quality was shown in the table 3 the cps values and the RSD for each point of RF power.

	850W		***900W***		***950W***		***1000W***	
	cps	RSD (%)	cps	RSD (%)	cps	RSD (%)	cps	RSD (%)
^{235}**U**	377.2	10.91	362.6	7.37	416.3	9.29	773.7	7.62
^{238}**U**	151464.3	7.49	147520.3	7.51	159638.8	3.90	336927.2	5.44

Table 3: Consolidated data from RF power adjustment.

Based on these experiments it was established the 1000 W as the work power. It can be verified analyzing the table 3, which shows that greater cps value for the ^{235}U and ^{238}U occurred at 1000W.

The next parameter to be evaluated was the z axis position (defocusing). The results are presented in the figure 3.

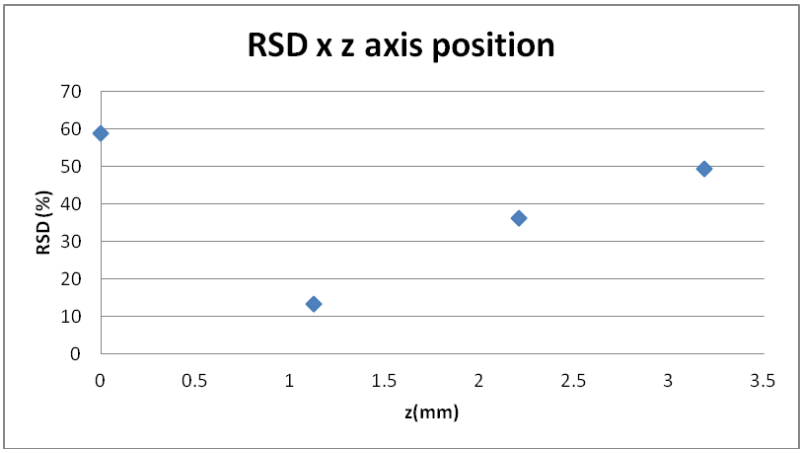


Figure 3: Adjustment data for z axis position above the sample surface.

When observing the figure 3 was noticed that a the z axis position at 1.125 mm showed the best RSD for the NIST 610 glass and was considered as a optimum optical position. This defocusing makes sense, since ablation on the sample surface carries out less particles into the plasma, which causes less interference in its stability. Keeping this parameter constant was varied the spot size of the laser ablation system.

To compare the signal quality was shown in the table 4 the cps values and the RSD for each point of z axis position.

	0 mm		***1.125 mm***		***2.205 mm***		***3.285 mm***	
	cps	RSD (%)	cps	RSD (%)	cps	RSD (%)	cps	RSD (%)
^{235}**U**	26.7	54.24	409.2	11.87	612.7	33.73	8.1	69.66
^{238}**U**	11624.5	34.55	178375.9	7.17	204370.4	7.61	5995.1	50.61

Table 4: Consolidated data from z axis (defocusing) adjustment.

Based on these experiments the point 1.125 mm above the surface was defined as the work defocusing. It could be verified analyzing the table 4, which shows that the best RSD value occurs for both, ^{235}U and ^{238}U, at the 1.125 mm defocusing. Although their cps value weren't the greatest, they presented the best RSD if compared with the others.

The last parameter to be evaluated was the laser beam diameter. The results were presented in the figure 4.

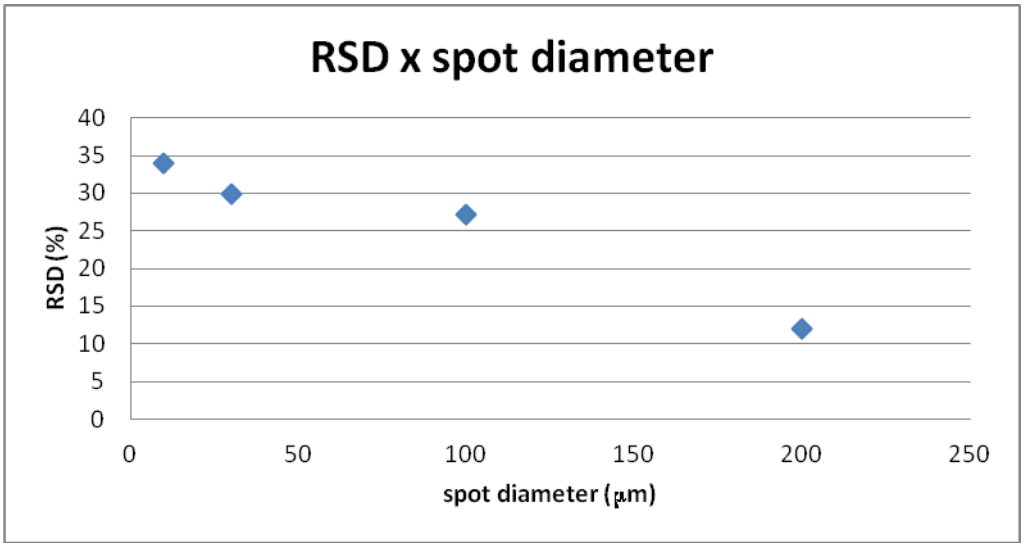


Figure 4: Adjustment data for spot diameter.

Observing the laser beam diameter adjustment (figure 4) was noticed that the diameter which had more stability was the 200 μm size. About this parameter was observed that the bigger the "spot" size the less is the RSD, probably due to lower energy density.

	10 μm		*30 μm*		*100 μm*		*200 μm*	
	cps	RSD (%)	cps	RSD (%)	cps	RSD (%)	cps	RSD (%)
^{235}**U**	45.0	56.00	108.3	40.86	247.5	27.33	386.7	9.22
^{238}**U**	17744.3	26.39	43520.1	13.31	88643.7	5.01	169466.8	6.25

Table 5: Consolidated data from laser beam diameter adjustment.

Based on these experiments it was established the 200 μm was the work laser beam diameter. It can be verified analyzing the table 5, which shows that the best RSD and cps values for ^{235}U occurs at the 200 μm diameter. Although their cps value weren't the greatest, they presented the best RSD if compared with the others.

Therefore, with respect to the adjustments parameters of RF power, z axis (defocusing) and laser beam diameter shown in the figures 2, 3 and 4 was concluded that a slow ablation with low energy density and beam defocusing improves the precision. These preliminary adjustments were of paramount importance to guarantee the sensibility and stability of the technique, avoiding to reach good precision and a relative standard deviation (RSD) between 1.55% to 7.60% for isotope ratio measurements, which is considered a reasonable value for laser ablation analysis. The values for adjusted parameters were set, as shown in table 1.

After the adjustments of the laser ablation system with the optimized parameters, the uranium pellet supplied and certified by News Brunswick Laboratory was analyzed and the results for isotope ratios of uranium were presented in the table 6:

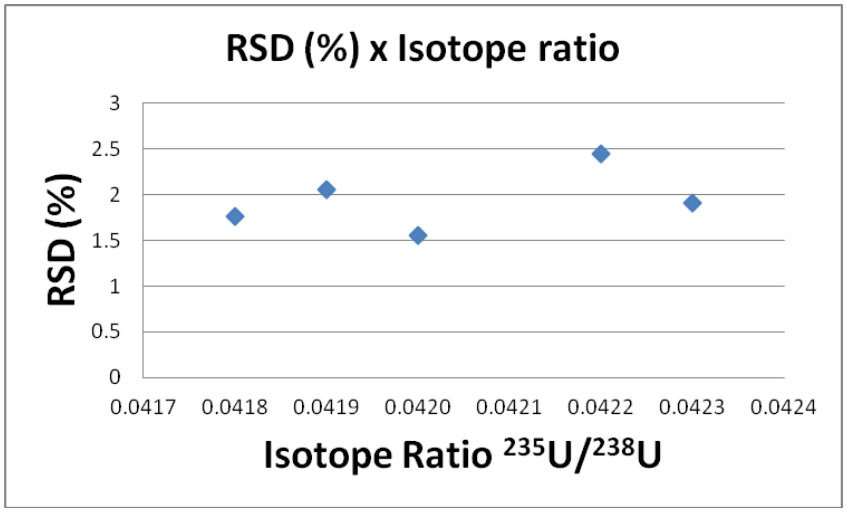
Isotope ratio ^{235}U/^{238}U	**RSD (%)**
0.0420	1.55
0.0418	1.76
0.0422	2.45
0.0423	1.91
0.0419	2.06

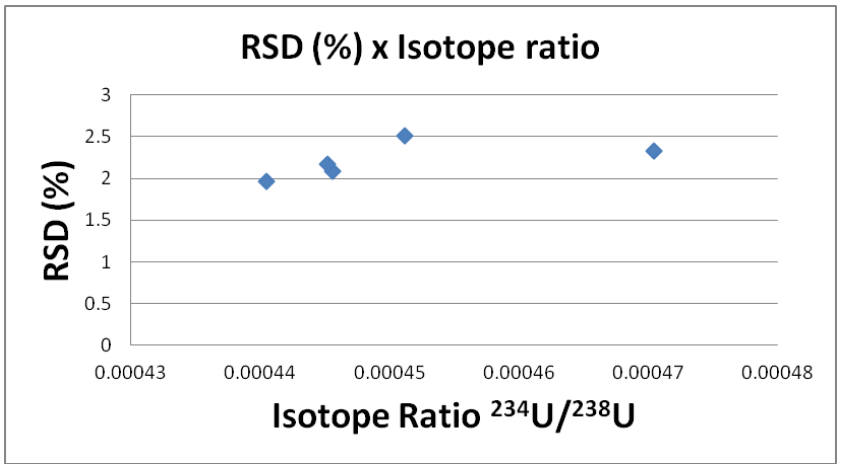
Isotope ratio ^{234}U/^{238}U	**RSD (%)**
0.00045	2.08
0.00044	1.96
0.00045	2.17
0.00045	2.33
0.00047	2.51

Isotope ratio ^{236}U/^{238}U	**RSD (%)**
0.000036	7.60
0.000033	6.14
0.000030	6.25
0.000033	6.14
0.000030	6.25

Table 6: Isotope ratios measurements.

Based on the table 6 were plotted the graphics for RSD versus isotope ratio, that were presented on figures 5.





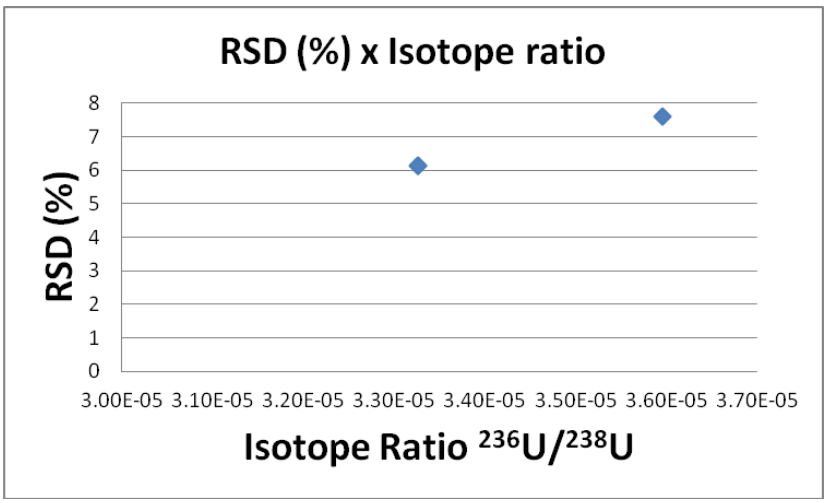


Figure 5: Isotope ratio stability.

According to figure 5, the $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotope ratios showed great stability, demonstrating the great strength of the LA-HR-ICP-MS technique. The $^{236}U/^{238}U$ showed more instability probably due its low concentration. Even the Laser Ablation process itself shows instability greater than the liquid sample introduction to isotope ratios measures, due to its intrinsic characteristics it has many other advantages compared to the liquid sample introduction, besides its good precision down to 0.005% [2]. When calculated the average of the results presented in table 6 were found the following values shown in table 7.

Isotope ratio	
$^{235}U/^{238}U$	$(4.20 \pm 0.44)x10^{-2}$
$^{234}U/^{238}U$	$(0.04 \pm 0.05)x10^{-2}$
$^{236}U/^{238}U$	$(0.00032 \pm 1.45)x10^{-2}$

Table 7: The measured isotope ratio of the investigated pellet.

After calculate the averages of the measurements, the atomic fraction must be calculated by the following expressions:

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

$$F_{235} = 100\,x\,\frac{\frac{^{235}U}{^{238}U}}{1+\frac{^{234}U}{^{238}U}+\frac{^{235}U}{^{238}U}+\frac{^{236}U}{^{238}U}} \quad (2)$$

$$F_{236} = 100\,x\,\frac{\frac{^{236}U}{^{238}U}}{1+\frac{^{234}U}{^{238}U}+\frac{^{235}U}{^{238}U}+\frac{^{236}U}{^{238}U}} \quad (3)$$

Where,

F_{234} = atomic fraction for ^{234}U isotope,
F_{235} = atomic fraction for ^{235}U isotope,
F_{236} = atomic fraction for ^{236}U isotope,
$^{234}U/^{238}U$ = isotope ratio between $^{234}U/^{238}U$,

$^{235}U/^{238}U$ = isotope ratio between $^{235}U/^{238}U$ and
$^{236}U/^{238}U$ = isotope ratio between $^{236}U/^{238}U$.

In order to evaluate the isotope ratios measurements and compare to the certified value were calculated the atomic fraction given by (1), (2) and (3). Their results were shown in the table 8.

Isotope ratio	
$^{235}U/^{238}U$	$(4.03 \pm 0.44)x10^{-2}$
$^{234}U/^{238}U$	$(0.038 \pm 0.049)x10^{-2}$
$^{236}U/^{238}U$	$(0.00031 \pm 1.45)x10^{-2}$

Table 8: Percent atoms abundance.

Taking the certificated value (table 2) for UO_2 pellet were calculated its isotope ratio, which was shown in table 9.

Isotope ratio	
$^{235}U/^{238}U$	$(4.2306 \pm 0.0029)x10^{-2}$
$^{234}U/^{238}U$	$(0.0389 \pm 0.0028)x10^{-2}$
$^{236}U/^{238}U$	$(0.0003 \pm 0.0002)x10^{-2}$

Table 9: Certified isotope ratio.

In order to evaluate the uranium isotope ratios between the certificated value and the measured value were calculated the isotope fractionation factor, which is a physical phenomenon that brings differences between the real isotope ratio value and the measured. It is associated to the preferential transport of the lightest isotope [4]. In the case of the time independent sample introduction this factor is given by:

$$F_{Discr} = \frac{R_{cert}}{R_{med}} = 1 + \alpha.n \quad (3)$$

Where,

F_{Discr} = isotope fractionation factor;
R_{cert} = certified isotope ratio;
R_{med} = measured isotope ratio;

α = error per mass unity and
n = mass difference.

Based on the data showed in table 9 were determined the isotope fractionation factor by the equation (3), which is sown in table 10.

Isotope ratio	F_{Discr}
$^{235}U/^{238}U$	1.0073
$^{234}U/^{238}U$	0.9725
$^{236}U/^{238}U$	0.9803

Table 10: Isotope fractionation factor.

Considering the global correction factor (K) as the average between those discrimination mass factor presented in table 6 and its value was K = 0.987 ± 0.017. This result shows great accordance with the expected value 1, within three times uncertainty, which means a linear behavior. Therefore, correcting this value by the K factor, the isotope ratio found for the isotope ratios were shown in table 11. These results are in agreement with those certified by New Brunswick Laboratory (NBL), within their uncertainty, besides their high uncertainty caused by instability of the laser ablation system.

Isotope ratio	
$^{235}U/^{238}U$	$(3.98 \pm 0.44)x10^{-2}$
$^{234}U/^{238}U$	$(0.038 \pm 0.049)x10^{-2}$
$^{236}U/^{238}U$	$(0.00031 \pm 1.45)x10^{-2}$

Table 11: Isotope ratio calculated by the global correction factor.

The corrected values (table 11), considering their uncertainties, was the same that the measured, because de correction factor is almost 1. However, if considered only the calculated value without their uncertainties, that carries the instability of the system, the results were $4.1958x10^{-2}$ for the $^{235}U/^{238}U$ isotope ratio, $0.03996x10^{-2}$ for the $^{234}U/^{238}U$ isotope ratio and $0.00032x10^{-2}$ for the $^{235}U/^{238}U$ isotope ratio. Nevertheless, even considering the uncertainty, the result was compatible with the certified value and could be comparable with those measurements made by Zsolt Varga, that reaches $(2.75 \pm 0.14)\times10^{-2}$ for natural uranium particle [3], once the order of magnitude of the uncertainty was the same reached in this paper.

3. CONCLUSIONS

The results obtained in this work demonstrated the capability of the Laser Ablation High Resolution Inductively Coupled Plasma Mass Spectrometry (LA-HR-ICP-MS) technique for

measurements of uranium isotope ratios in pellet samples. The results found were in good agreement with the certified values reaching $^{235}U/^{238}U$ isotope ratio of $(3.98 \pm 0.44)x10^{-2}$ and a RSD between 1.55% to 2.45% against $^{235}U/^{238}U$ isotope ratio of $(4.2306 \pm 0.0029)x10^{-2}$ certified by New Brunswick Laboratory. Nevertheless, there is a need to improve the signal stability of this powerful technique in order to reach a low uncertainty level, once the main advantage of this method is to preserve the testimonies, what is very useful for safeguards and nuclear forensic purposes.

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