^{235}U/^{238}U ISOTOPIC RATIO MEASUREMENTS IN REFERENCE MATERIALS BY USING THE HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT

Uranium isotopic ratio analyses with nuclear concern is usually done by dedicated mass spectrometers, mainly those based on thermal ionization source (TIMS). In this work, a mass spectrometer using a inductively coupled plasma as a source of ions with a Nier-Johnson reverse geometry analyzer (High Resolution Inductively Coupled Plasma Mass Spectrometer, Finnigan MAT Element, Bremen, Germany) was used in order to analyze uranium compound and determine the isotopic ratios of the isotopes ^{235}U and ^{238}U. The NBS500 certificate material (National Institute for Standards and Technology, NIST, former National Bureau of Standards, NBS) was analyzed along ten days to obtain more consistent data. The results showed good agreement with the certificate and with TIMS results. Results for NBS 200 and 030 are also presented for discrete days.

Key Words : uranium, isotopic ratio, inductively coupled plasma mass spectrometry, reference material.

I. INTRODUCTION

It is well known that the contemporary life style is totally dependent on energy production. The energy is mainly consumed in electrical and thermal forms. In order to provide the energy needed to the human consumption, and the growing demand, different sources of energy production are available by now [1]. Among these sources of energy production, nuclear power generation is one of the majors and attractive ways to produce electric energy wherever the demand is. Uranium has been used as nuclear fuel since the first nuclear reactor by Fermi in the Chicago University almost 50 years ago. Since that, many studies have been dedicated to increase the knowledge about this element having no equal efforts, and results, in such a short period of time in any part of the mankind's history. However, as a controversial source of energy production it is, the nuclear way is still in constant studies providing more and more information to be established firmly under our eyes. Depending on the nuclear power reactor concept, the enrichment level of ^{235}U in the nuclear fuel varies from the natural abundance, 0,72%, to more than 20 %, by weight. Traditionally, mass spectrometers with thermal ionization ions source (TIMS) are used to analyze the uranium isotopic abundance in these nuclear fuels [2,3]. After all these years of development and due the nature of this source, TIMS provides very accurate and precise results for uranium isotopic ratio determination. In the 80's, a new concept of mass spectrometers based on plasma ion source (inductively coupled plasma, the ICP) emerged bringing renewed breeze to this field of isotope analyses. They are the inductively coupled plasma mass spectrometers, ICPMS. Nowadays, the most common analyzer for ICPMS is the quadrupole that allows a very compact ion path and, consequently, small equipments. Due this concept, the measurements are precise and accurate, the sensitivity for the most of the elements is better than for ICPAES and AAS (atomic absorption spectrometry), and the time consumed in the instrument is shortened if compared to those techniques mentioned before. The isotopic ratio analyses can be carried out in the quadrupole ICPMS depending on whether the mass to charge ratio (m/z) has no isobaric interferences in the concerned isotopes. In 1995, a new concept analyzer ICPMS was introduced commercially, the Finnigan MAT Element, named high resolution inductively coupled plasma mass spectrometer, HR-ICPMS. Its Nier-Johnson reversed geometry analyzer (magnetic followed by

electrostatic field) with a grounded interface allows to reach actual resolution of 9000 (m/Δm). As a consequence, several isobaric interferences can be overcome just changing the resolution from a lower to a higher one. For instance, the very known isobaric interference $^{40}Ar^{16}O/^{56}Fe$ can be resolved in nominal resolution of 3000. This concept of analyzer produces precise and accurate measurements, with sensitivity compared to those based in the quadrupole or better and also very short time consuming. ICP mass spectrometers run samples in liquid form with constant intake of the solution. This is a great feature as one can analyze samples in this more homogeneous physical state. As many isobaric interferences are resolved in the analyzer, there are no need of long sample chemical treatments and skilled operators, as needed when using TIMS. Some applications of this analyzer concept in isotopic ratio analysis have been reported in the literature by Vanhaecke et alii [4,5]. For very precise applications one has to use TIMS preferable with multicollector. A rapid comparison between TIMS and ICPMS features in isotope analysis is given by Schmidt in [6].

In this work, different uranium samples were analyzed in order to determine the isotopic ratios of the isotopes ^{235}U and ^{238}U. The NBS 500 certificate material (National Institute for Standards and Technology, NIST, former National Bureau of Standards, NBS) was analyzed along ten days to obtain more consistent data. Optmized instrumental parameters were obtained for each day and are discussed, as well.

II. EXPERIMENTAL SECTION

Equipment. The uranium isotopic ratios were obtained using a Finnigan MAT Element inductively coupled plasma mass spectrometer, HR-ICPMS, (Finnigan MAT, Bremen, Germany) at the laboratory of the Grupo de Caracterização Isotópica - GCI of the Instituto de Pesquisas Energéticas e Nucleares - IPEN, Comissão Nacional de Energia Nuclear, CNEN, São Paulo, Brazil. The mass spectrometer analyzer is based on the reversed Nier-Johnson Geometry with a grounded interface. The ion path comprises first a region within a magnetic field followed by another one within an electrostatic field. This geometry associated to three different slits gives the nominal resolution of 300 (low resolution), 3000 (medium resolution) and 7500 (high resolution). In this work we used the low resolution mode (m/Δm = 300). Mass ranges used for the ^{235}U and ^{238}U were 235.024 – 235.064 and 238.031 – 238.071, respectively.

All the measurements were carried out in a free aspiration mode using a Meinhard® concentric nebulizer (J. E. Meinhard Associates Inc.), and a Scott-type spray chamber maintained at 4-5 °C using a closed circuit refrigeration system (Typ 0001, Van der Heijden). Power

was supplied by a 27 MHz radio-frequency generator (ICP20, RF Power Products). Standard conditions are summarized in the TABLE 1.

TABLE 1. Finnigan Element HR-ICPMS Standard Conditions for Uranium Isotopic Analyses in Low Resolution Mode.

Radio Frequency (rf power), W	1330
Argon flow rates, L/min[a]	
External	15
Intermediate	1.3
Internal	1.1
Sample Uptake, L/min[a]	0.8
Sample Cone and Skimmer	Nickel

a. Gas flow and sample uptake optimized conditions vary for each nebulizer used.

Solutions. NBS500 reference material was used to setup the experimental conditions. All the solutions were prepared with nitric acid (SupraPur®, Merck) and Milli-Q® water. Whenever possible, the most abundant isotope concentration was 10 μg/L. Acid concentration was maintained at 5 %, v/v, in all cases. No internal standard was added. Sample fresh solutions were prepared just before the measurements.

Blanks. No blank correction was necessary because the real blank intensities for the uranium isotopes were too low, less than 500 cps whatever isotope concerned. No significant memory effect was found for uranium isotopes in previous studies.

Measurements. Experimental conditions associated to sample solution concentration were established in order to obtain signal intensities not lower than 20,000-30,000 counts per second, cps, and not higher than 2×10^6 cps for the most abundant isotope. As the ^{235}U and ^{238}U abundances are almost the same in the NBS500, all the analyses were carried out measuring peak intensities between 1 and 2×10^6 cps. Discussion about improving RSD with increasing cps is presented by Vanhaecke [5]. For the temporal analyses the number of scans were 750 performing 4.5 min, approximately. The daily uranium isotopic ratio value is a result of ten 4.5 min measurements of each sample. The integration window, that is, the real mass interval used to measure the isotopes intensities, was 5 % of the peak width. The flat top condition associated to this integration window allows measuring the best region of the peak.

Data Acquisition. The Finnigan Element ICPMS is controlled by an on-board computer. The interface with the operator is a Pentium® 100 based personal computer

running a Windows NT® operating system. Almost all instrument conditions; including lens, gas flow, rf power and others; have to be setup using this controlling software. Data acquisition was run under optimized conditions to obtain the best accuracy and precision for the uranium isotopic ratios. These conditions are presented in TABLE 2.

TABLE 2. Data Acquisition Best Conditions for $^{235}U/^{238}U$ Isotopic Ratio Measurements in the Finnigan Element HR-ICPMS.

Integration Mass Window	5 %
Mass Range[a], u	
^{235}U	235.024 – 235.064
^{238}U	238.031 – 238.071
Number of Samples	300
Sample Scanning Time, s	0.0100
Number of Scans	750
Scan Duration, s	0.150
Scan Type	E-Scan[b]
Total Measurement Time, min	4.5
Detection Mode	Counting[c]

a. Actual integration mass range integrated using the 5 % selection.
b. Fixed magnetic and variable electrostatic field.
c. Finnigan Element HR-ICPMS secondary electron multiplier detection mode

III. RESULTS AND DISCUSSION

Instrumental Standard Conditions. In order to obtain the best condition for uranium isotopic ratio analysis, several parameters such as, rf power, sample introduction system (Meinhard or micro-concentric nebulizers), peristaltic pump aided or free aspiration, argon flow rate, sample uptake, and settings of all lenses in the path into the analyzer. Radio frequency power has great influence in the uranium isotopic ratio values. As can be seen in Fig. 1 the values for the $^{235}U/^{238}U$ ratio in NBS500 reference material increase as the rf power increase as well. No clear reasons was found in the literature to explain it, although high temperatures and the well defined plasma regions yielded in the higher rf power conditions seem to be indications of this behavior. Ting and Janghorbani [7] made some studies varying the rf power supply, although no conclusive discussion was presented.

The optimized lens settings produce a well defined flat top peak in the low resolution mode. In isotopic analysis a flat top peak condition is essential to obtain precise measurements and just 5 or 10 % of the peak top is measured in each mass because the peak tails are prone to higher instabilities. If this condition could not be adjusted

poor data can be generated even integrating 5 % of peak
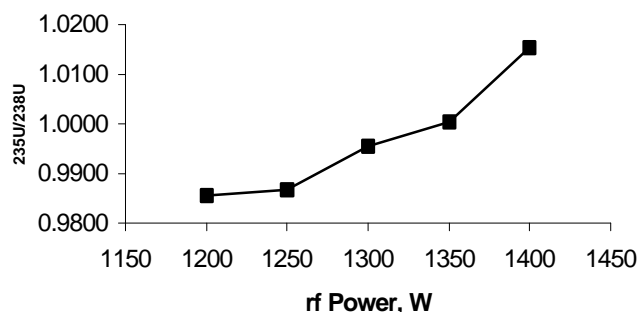
top.

Figure 1. $^{235}U/^{238}U$ Isotopic Ratio Dependence on RF Power Supply in the Finnigan Element HR-ICPMS. NBS 500 reference material certified value is 0.9997.

Data Acquisition. Data acquisition defines the quality of the results and can be consider as instrumental conditions. After have adjusted peak shape the parameters were setup to the optimized conditions. This procedure is almost a try and error sequence, because the instrument software does not permit the on-line data acquisition optimization.

Applying the conditions showed in TABLE 2 high precision data can be generated. In an ideal situation once setup the optimized conditions the instrument performance must not change for long periods. However, the lens settings have to be checked daily and, sometimes, even the mass calibration has to be run during the analysis. However, the mass calibration stability was good enough to be run only once in the mornings of each day.

Integration mass window was setup as 5 % of peak width. Since 10 % window gave same precision, the 5 % window was chosen as time analysis could be saved. The number of samples was chosen in order to measure neither excessively or poorly. With an excessive number of samples the analysis is time consuming and no significant improvement can be reached, and with few numbers of samples information of the peak can be lost. This approach can be extended to the number of scans and to the sample scanning time. The E-Scan was chosen because for this specific instrument it was scanning type, which gave the best precision results. The other two scanning types are B-Scan and Synchro—Scan, magnetic and magnetic and electrostatic varying fields, respectively. The detector used in the Finnigan Element ICPMS is a secondary electron multiplier, SEV. The instrument can detect the ions with two distinct modes using the same detector. In the Analog mode 7 of the dynodes are used to multiply the signals so high cps between 10^4 and 10^{10} can be measured. The Counting mode uses all the 19 dynodes but signal measurements are limited to 5×10^6 cps. This feature allows measuring low concentration signals with few or no background noise as no useful inputs are multiplied.

These several parameters can not be understood and controlled as a whole at first sight. The time demanded to understand all these instrumental parameters is long and the considerations about them are not the main interest of the present work.

Uranium Isotope Ratios. Uranium isotopic ratio analyses have been usually done by TIMS for a long time as this technique gives very accurate and precise results. ICP based mass spectrometry is a relatively new technique, if compared to TIMS, but have been providing results precise enough to fulfill the requirements for nuclear concerns. This can be seen in the results of the present work, shown in TABLE 3, obtained with a high resolution inductively coupled plasma mass spectrometer for three different reference materials, as follow, NBS 500, 200, and 030.

TABLE 3. $^{235}U/^{238}U$ Ratios Obtained for NBS 500, 200, and 030 Reference Materials Using the Finnigan Element HR-ICPMS.

Reference Material	$^{235}U/^{238}U$ Ratio ± RSD (%)[a]	Certified Value[b]
NBS 500	0.9937 ± 0.07	0.9997 ± 0.1
NBS 200	0.2487 ± 0.11	0.25126 ± 0.1
NBS 030	0.0349 ± 0.14	0.03143 ± 0.1

a. Ten samples average.
b. RSD for the certified values is at least 0.1 percent.

Reliable results are achieved when precise long term values for isotopic ratios are obtained. These experiments were performed in order to evaluate the robustness of the methodology. TABLE 4 shows NBS500 $^{235}U/^{238}U$ average value of 0.9968 with relative standard deviation (RSD) of 0.5 % obtained during ten non-consecutive days. This is a very good result considering that the certified value is 0.9997 using TIMS. The RSD values for each day is around 0.1 % with high values (0.2 and 0.3 %) in two of these days. If compared to routinely TIMS analyses the RSD is a little bit high. The last ten measurements for this material obtained with TIMS (Varian MAT TH5) in our laboratory gave for this ratio an average value of 1.0036 with a RSD of 0.2 %. The isotopic ratio and its precision can significantly be changed if the peak shape will not be well adjusted. As this adjustment is a matter of operator's skills, the poorest results can be improved if this source of error could be evaluated by using temporal analyses.

NBS 500 is the most appropriate reference material used for this purpose because the abundance of these two isotopes are almost the same (see Table 3) reducing isotopic fractionation when analyzing in mass spectrometry. The error in the NBS 200 and 030 $^{235}U/^{238}U$ results can, somehow, be associated to this phenomenon.

Isotopic mass fractionation is related to the fundamentals of mass spectrometric techniques. This always occurs as the isotope m/z ratios behave differently under the magnetic and electrostatic fields. The value can be calculated using reference materials correcting the result when necessary. No such a correction was applied in the results showed in this work.

TABLE 4. $^{235}U/^{238}U$ Ratios (n = 10) Obtained for NBS 500 Reference Material Using the Finnigan Element HR-ICPMS.

Date	$^{235}U/^{238}U$ Value	RSD, %
06/05	0.9964	0.2
07/05	0.9937	0.1
11/05	1.0013	0.1
12/05	0.9965	0.1
13/05	0.9915	0.1
14/05	0.9908	0.1
17/05	0.9907	0.1
19/05	1.0025	0.3
25/05	0.9937	0.1
26/05	1.0013	0.1
Average	0.9958	
RSD, %	0.45	
Certified Value	0.9997	

IV.   CONCLUSION

The methodology used in this work is very simple and does not require special skills. Starting from the powder material, all one needs is to turn it into solution and dilute it to an appropriate uranium concentration in a 5 % nitric acid medium. No other treatment, such as chemical separation, is needed. As the most of uranium compounds are very easy to dissolve in nitric acid medium, this is a fast procedure in comparison to the traditional TIMS analysis.

This procedure is now being applied to the analysis of more complex matrix samples and with different uranium isotope abundances.

The results presented in this study show that the $^{235}U/^{238}U$ determination using the HR-ICPMS can be done in samples with uranium isotopic ratios similar to those analyzed materials. Very good precision values were obtained using the standard conditions and short time analyses. Higher sample throughput can be reached as no special chemical treatment is necessary and due to the ICP physical features allowing more samples to be analyzed if compared to TIMS with needed data quality. Further studies are being carried out in order to establish the best experimental condition to analyze together the major, ^{235}U and ^{238}U, and the minor, ^{234}U and ^{236}U, isotopes.

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