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URANIUM ISOTOPES DETERMINATION IN URINE SAMPLES USING ALPHA SPECTROMETRY AND ICP-MS

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ABSTRACT

The action of determining the concentration of uranium isotopes in biological samples, "in vitro" bioassay, is an indirect method for evaluating the incorporation and quantification of these radionuclides internally deposited. When incorporated, these radionuclides tend to be disposed through excretion, with urine being the main source of data because it can be easily collected and analyzed. The most widely used methods for determination of uranium isotopes (^{234}U, ^{235}U and ^{238}U) are Alpha Spectrometry and ICP-MS. This work presents a comparative study for the determination of uranium isotopes using these two methodologies in real samples from occupationally exposed workers. In order to validate the methodology, a sample of the intercomparison exercise organized by PROCORAD (*Association pour la promotion du controle de qualite des analyses de biologie medicale em radiotoxicologie*) was used, and the results were statistically compared applying the Student's t-test.

Keywords: Uranium Isotopes, Alpha Spectrometry, ICP-MS.

1. INTRODUCTION

The primary goal of occupational radiation protection is to achieve and maintain acceptable and satisfactory working conditions in the nuclear fuel cycle facilities.

Workers who perform activities in controlled areas, where there is a chance of incorporation of radioactive material in normal operating conditions, need to be followed up by a program that, among other things, involves the internal individual monitoring of employees. This monitoring can be performed by [1]:

- Measurements in biological samples - *in vitro* (urine, feces and other complementary ones);
- Measurements in physical samples (air filter - individual lapel dosimeter);
- Direct measurements - *in vivo* (whole body, organs and tissues) [1].

The "*in vitro*" bioassay is an indirect method that identifies and quantifies internally deposited radionuclides, through analysis of biological material (urine and feces) [1]. The choice of biological material to be analyzed depends on the main route of excretion of the radionuclide in question; in general, urine samples are easy to be collected and analyzed, being the basis for determining the uptake of readily absorbed materials, and also allowing to estimate the systemic activity levels in body tissues [2].

This paper presents a comparison between two methods used for determination of uranium isotopes in urine samples from occupationally exposed workers: Alpha Spectrometry and ICP-MS (Inductively Coupled Plasma Mass Spectrometry). The analyses were performed in the Pocos de Caldas Laboratory of the National Nuclear Energy Commission (CNEN / LAPOC), and the samples of intercomparison tests promoted by PROCORAD (*Association pour la promotion du controle de qualite des analyses de biologie medicale em radiotoxicologie*) were used for validation of the methodology.

2. MATERIALS AND METHODS

Eleven urine samples from occupationally exposed individuals, collected in a 24-hour period, were selected for analysis. The samples were homogenized, an aliquot of 10 mL was separated for determination by ICP-MS, and the remainder was used for determination by Alpha Spectrometry.

2.1. Determination of uranium by ICP-MS

Uranium can be isotopically determined using the ICP-MS technique and, due to the low sensitivity of the ^{234}U isotope, this one was not included when interpreting the statistics.

In this method, the sample is subjected to analysis on diluted liquid form, with low quantity of dissolved salts, where the ions formed are registered, and the response of the equipment provides the mass spectrum that relates the isotopic abundance and distribution of uranium isotopes [3].

1 ml aliquot of the sample was used for the analysis, diluted using 5% of HNO_3 at a ratio of 10:1. To ensure the quality of the measurement by ICP-MS (NexION 300X - PerkinElmer), the counting of 1ml of the internal standard of Indium 0.25 $\mu g.L^{-1}$ was performed before the sample counting. The reading of this standard indicates losses due to waste excess, causing the clogging of the equipment hoses when carrying out the necessary measurements.

2.2. Determination of uranium by Alpha Spectrometry

The uranium isotopes were quantified in an Alpha Spectrometer model Alpha Analyst from Canberra Industries, with semiconductor surface-barrier detector.

The determination of uranium by Alpha Spectrometry requires a separation and previous purification of this element, as well as obtaining an adequate source for the measurement. The method used in this work is described in the following steps:

2.2.1 Pre concentration of the sample by coprecipitation

The remaining volume of each sample was measured and entirely used for the coprecipitation, in which 0.04 Bq of ^{232}U tracer was added for determination of the uranium chemical recovery.

30 mL of H_2O_2 was added to the sample, which was taken into heating on an electrical plate until obtaining a light yellow color, then 200 uL of ammonium hydrogen phosphate and 4

drops of phenolphthalein indicator were added. Time was given for cooling until about 70-80°C and, under stirring, the sample was precipitated with NH_4OH until the color change of the indicator happened; if precipitation did not occur, 1 mL of $Ca(NO_3)_2$ 1.25 mol.L^{-1} was added.

The sample was allowed to decant until the following day. The supernatant was then siphoned and the precipitate was diluted in half HNO_3 3 mol.L^{-1}.

2.2.2 Uranium radiochemical separation

The sample solution was percolated into the chromatographic columns UTEVA Eichrom® [4] pre conditioned with HNO_3 3 mol.L^{-1}. The effluent was discarded, then 10 mL of HCl 9 mol.L^{-1} were percolated through the resin for modification in acidic medium; this effluent was also discarded, and the uranium was eluted with HCl 0.01 mol.L^{-1}.

The effluent was dried in a heater plate and the salts obtained were dissolved with H_2SO_4 3 mol.L^{-1} and ammonium sulfate 0.8 mol.L^{-1}.

2.2.3 Electroplating and quantification of uranium

The samples were electroplated on polished silver plates, under electric current of 1.2A for 60 minutes.

For quantification of uranium isotopes in the Alpha Spectrometer, energies of 4.31 MeV were used for the traces of ^{232}U, 4.74 MeV for ^{234}U, 4.47 MeV for ^{235}U and 4.19 MeV for ^{238}U. The samples were counted during 200000 seconds.

3. RESULTS AND DISCUSSION

The results of the urine samples obtained by Alpha Spectrometry and ICP-MS for determination of ^{234}U, ^{235}U and ^{238}U in occupationally exposed workers are presented in Table I.

The *Student's t-test* statistical test was used, which is the one utilized to compare two paired samples. The tests presented *p-values* greater than 0.05 for both determinations of radionuclides, proving that there is no significant difference between the methodologies applied for determination of uranium isotopes in urine samples.

The mean, standard deviation, *t-test* and *p-value* of the statistical tests for comparison of the methodologies to determine the ^{235}U and ^{238}U isotopes are presented in Table II.

For better visualization of the data comparison of the methodologies used, scatter plots are presented in relation to the activity concentrations of ^{235}U and ^{238}U, in Figures I and II.

Table I. Results of the determination of uranium isotopes in urine samples.

	^{234}U (mBq.L^{-1})		^{235}U (mBq.L^{-1})		^{238}U (mBq.L^{-1})	
	ICP-MS	**Alpha Spec.**	**ICP-MS**	**Alpha Spec.**	**ICP-MS**	**Alpha Spec.**
1	-	8.99 ± 1.03	0.65 ± 0.16	0.94 ± 0.28	1.29 ± 0.32	1.51 ± 0.36
2	-	31.70 ± 3.23	1.20 ± 0.30	2.07 ± 0.52	1.31 ± 0.33	1.03 ± 0.36
3	-	12.50 ± 0.93	0.76 ± 0.19	0.69 ± 0.17	0.92 ± 0.23	0.98 ± 0.20
4	-	89.10 ± 4.05	3.36 ± 0.84	4.36 ± 0.34	2.34 ± 0.59	2.38 ± 0.23
5	-	1.32 ± 0.25	<0.40	< 0.30	0.53 ± 0.13	0.82 ± 0.19
6	-	0.71 ± 0.17	<0.40	< 0.27	0.24 ± 0.06	0.56 ± 0.15
7	-	0.43 ± 0.12	<0.40	< 0.22	0.32 ± 0.08	0.52 ± 0.12
8	-	0.40 ± 0.15	<0.40	< 0.30	0.56 ± 0.14	<0.31
9	-	0.97 ± 0.21	<0.40	0.45 ± 0.14	0.62 ± 0.16	0.88 ± 0.19
10	-	0.35 ± 0.10	<0.40	< 0.20	0.49 ± 0.12	0.23 ± 0.08
11	-	1.16 ± 0.21	<0.40	< 0.31	0.64 ± 0.16	0.91 ± 0.18

Table II. Values of mean, standard deviation, *t-test* and *p-value* for the 11 samples analyzed with 10 degrees of freedom.

Isotope	**Alpha Spectrometry**		**ICP-MS**		***t-test***	***p***
	Mean	**Deviation**	**Mean**	**Deviation**		
^{235}U	0.92	1.26	0.80	0.89	0.96	0.36
^{238}U	0.92	0.60	0.84	0.61	1.11	0.29

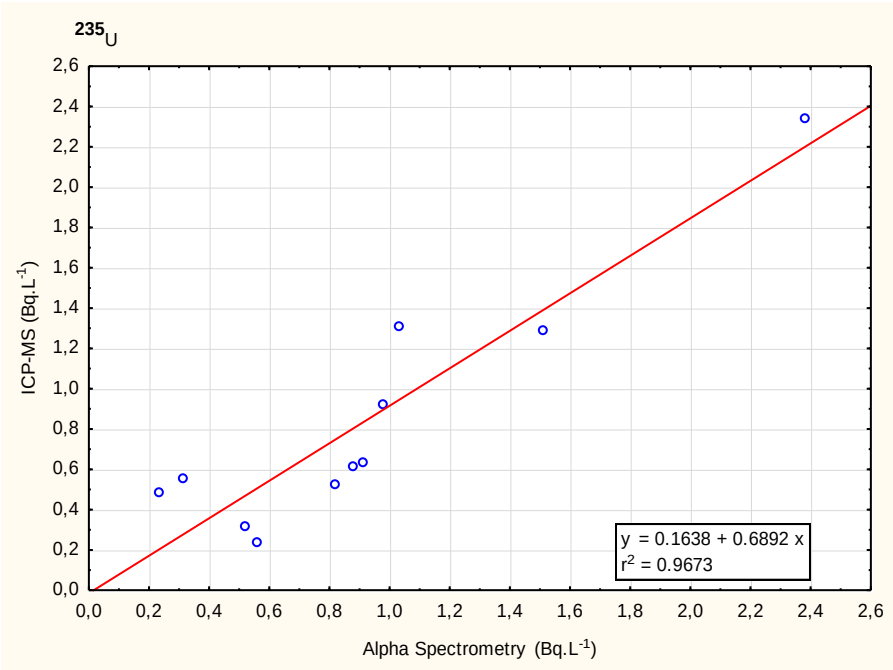

Figure I. Scatter Plot: comparison of methodologies between ICP-MS and Alpha Spectrometry for ^{235}U.

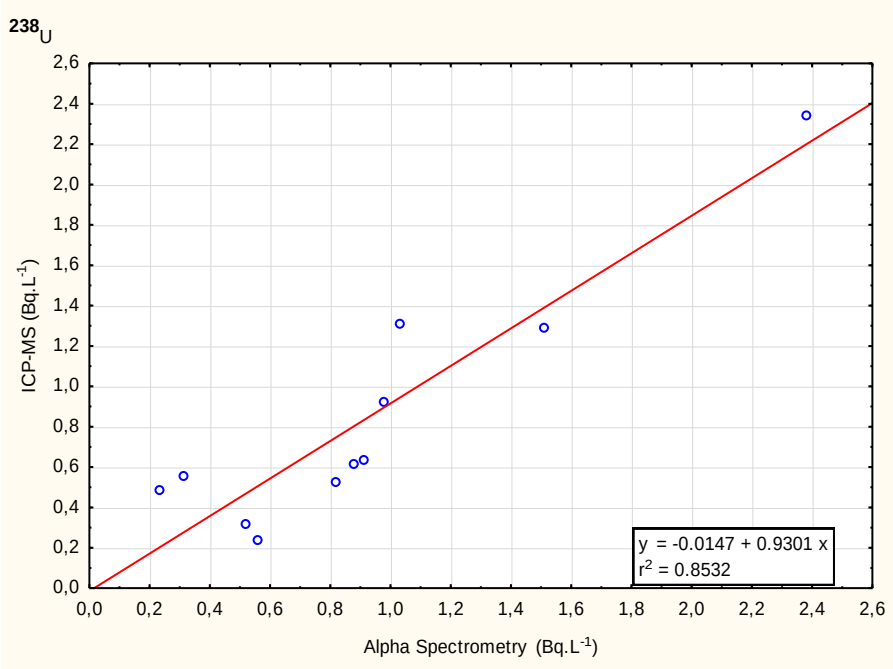

Figure II. Scatter Plot: comparison of methodologies between ICP-MS and Alpha Spectrometry for ^{238}U.

Table III presents the results of the methodology validation which was carried out with two samples of the intercomparison exercise promoted by PROCORAD in 2014.

Table III. Results of the intercomparison exercise promoted by PROCORAD.

	RN*	ICP-MS (µg.sample^{-1})		Espectrometria Alfa (Bq.sample^{-1})	
		Lab Result	Real Result	Lab Result	Real Result
A	^{234}U	-	1.05E-03 ± 6.0E-05	2.03E-01 ± 9.41E-03	2.42E-01 ± 1.40E-02
	^{235}U	1.37E-01 ± 2.75E-02	1.38E-01 ± 8.0E-03	1.01E-02 ± 1.05E-03	1.10E-02 ± 6.00E-04
	^{238}U	1.93E+01 ± 1.90E+00	1.95E+01 ± 1.10E+00	2.16E-01 ± 9.97E-03	2.40E-01 ± 1.40E-02
B	^{234}U	-	1.80E-04 ± 1.00E-05	3.48E-02 ± 1.68E-03	4.15E-02 ± 2.40E-03
	^{235}U	3.70E-02 ± 1.60E-02	2.55E-02 ± 1.50E-03	1.62E-03 ± 2.37E-04	2.04E-03 ± 1.00E-04
	^{238}U	2.95E+00 ± 5.00E-01	3.33E+00 ± 1.90E-01	3.79E-02 ± 1.80E-03	4.14E-02 ± 2.40E-03

*RN= Radionuclide

From the results obtained in the intercomparison exercise presented in the table above, it was possible to verify the good performance of the laboratory and the good accuracy of the method regarding the determination of radionuclides in both methodologies.

4. CONCLUSION

The concentration of uranium isotopes in biological samples, "in vitro" bioassay, can be evaluated when incorporated in the urine of occupationally exposed workers by applying two different methodologies: Alpha Spectrometry and ICP-MS.

Although the Alpha Spectrometry technique requires a refined chemical process in relation to the ICP-MS technique, that requires little treatment of the sample, both methods presented high precision and good accuracy in the results.

After statistical testing and validation using a sample of the intercomparison exercise promoted by PROCORAD, it was possible to conclude that both methods are suitable for determination of uranium isotopes in urine.

5. ACKNOWLEDGEMENTS

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