

DEVELOPMENT AND VALIDATION OF DETERMINATION OF URANIUM AND THORIUM IN WATER SAMPLES BY ICP-MS

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ABSTRACT

Determination of uranium (U) and thorium (Th) in water samples is an important parameter to the human exposure to drinking water consumption, especially in rural areas influenced by mining activities. Indeed, the Brazilian Ministry of Health has recently established guidelines of 0.03 mg L^{-1} for U in drinking water. However, adhering to such guidelines requires the development and validation of effective analytical techniques. Here, we directly address this requirement, presenting a methodology for determination of U and Th in drinking water samples by inductively coupled plasma mass spectrometry (ICP-MS). The methodology was validated through the analysis of Standard Reference Material 1640a (NIST), synthetic samples and data obtained during an inter-laboratory comparison program. The response curve derived from the method is linear, and the detection and quantification limits were $0.12 \text{ } \mu\text{g L}^{-1}$ and $0.29 \text{ } \mu\text{g L}^{-1}$ for U and $0.63 \text{ } \mu\text{g L}^{-1}$ and $1.7 \text{ } \mu\text{g L}^{-1}$ for Th.

1. INTRODUCTION

Drinking water is a basic human need and, beyond consumption, is used in numerous daily activities. To be considered safe for consumption, it typically has to conform to several quality standards defined by national government. For example, the Brazilian Ministry of Health has developed quality standards (Federal Ordinance n. 2914) that clearly define the level of toxic chemicals that are considered to represent a risk to human health. For the toxic radioactive metal uranium (U), the guideline value is 0.03 mg L^{-1} . Article 38 of the Ordinance defines the potability of water from the radiological perspective, defining the limits of activity as 0.5 Bq/L (Becquerel per liter) for total alpha activity and 1 Bq/L for total beta activity. However, these values only relate to the nuclides Ra^{226} and Ra^{228} [1] and no value for thorium (Th) is established in the document.

Radionuclides from uranium and thorium contribute about 70 % of the annual dose per person from exposure to natural radiation. However, the contribution of the U^{235} isotope to the total dose is very low and is not taken into account in determining dose [2].

Uranium and Thorium are occur naturally in soils, rocks and other materials, and can be easily transferred to the water and consequently incorporated into humans. The importance of these elements for human health is related to their chemical and radiological toxicity and decay products [3]. The objective of this study is therefore to determine and validate the presence and concentration of U and Th in water samples using inductively coupled plasma

mass spectrometry (ICP-MS). Validation is the verification, where the specified requirements are adequate for an intended use and is the important step to assure reliable analytical results [4]. Here, we validate using synthetic samples, standard reference material and participating in interlaboratory comparison.

2. METHODS

2.1. Instrumentation

A Perkin-Elmer NexION 300D inductively coupled plasma mass spectrometer (ICP-MS, Standard mode, PerkinElmer Inc., Waltham, MA, USA) was used for all measurements.

2.2. Method Validation

The parameters used to method validation were linearity, selectivity, detection and quantification limits, using standard reference material and participating in interlaboratory comparison.

Linearity was tested by constructing calibration curves. The curves were prepared with standard solutions of various concentrations (1, 5, 10, 20, 30 and 40 $\mu\text{g kg}^{-1}$) with 1% HNO_3 solution in Milli-Q water (18.2 $\text{M}\Omega\text{ cm}$, Millipore). These solutions were made by appropriate dilution, by mass, of a certified 1000 $\mu\text{g g}^{-1}$ U and Th stock solutions (ICP standard solutions, SPEX Industries).

A further curve was constructed using the same reference points, but using tap water with 1% HNO_3 solution, to confirm the selectivity of the method. NIST Standard Reference Material (SRM 1640a) with certified uranium concentration of 25 $\mu\text{g kg}^{-1}$ was used for validation.

Blank samples were prepared and analyzed to assure analytical control and for calculating detection and quantification limits.

2.3 Participating in Interlaboratory Comparisons

Samples from the Institute of Radiation Protection and Dosimetry (IRD, Brazil), part of the National Intercomparison Program, were analyzed. The preparation recommended by the supplier consisted of diluting in a ratio of 1:8 by adding 62.5 mL of the sample and completing to 500 mL with 1 % HNO_3 solution. Next, 0.3 g of indium (In) solution (internal standard) with a concentration equal to 50 $\mu\text{g kg}^{-1}$ was added with a plastic tube and completed to 10 g with diluted water.

3. RESULTS AND DISCUSSION

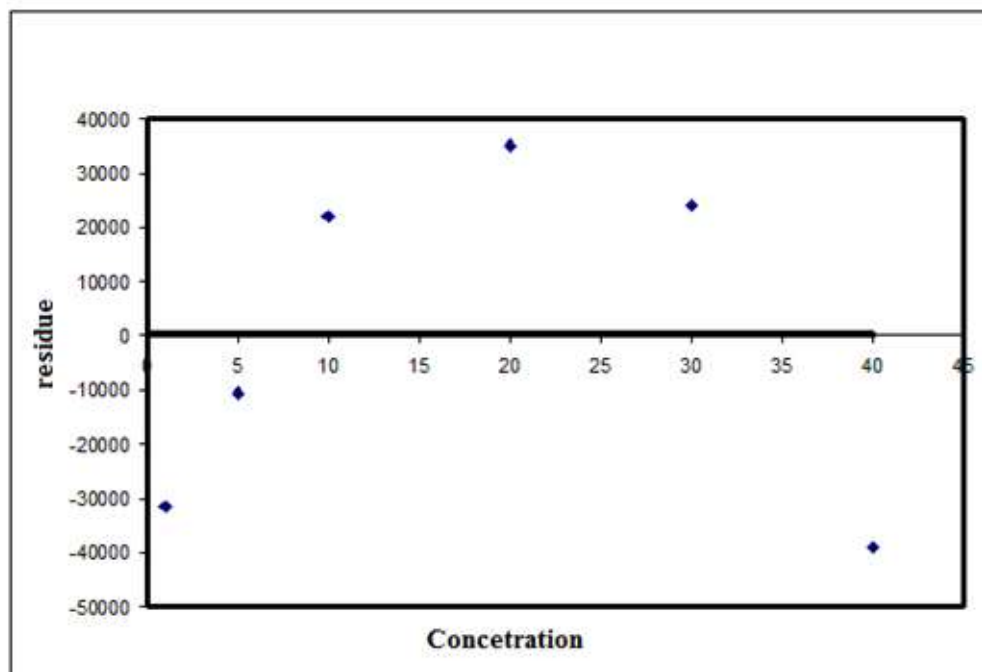
3.1. Linearity

The Table 1, show the results of the linearity tests from the results obtained through the calibration curve with Milli-Q water. Before this, was applied the Grubbs test and the results were satisfactory.

Table 1: Results for linearity tests

TEST	RESULTS	CONCLUSION
Significance of regression or validity of regression	$MQ_{reg}/MQ_r = 2050.6$ $F_{tabulated} = 7.71$	MQ_{reg}/MQ_r it is greater than $F_{tabulated}$ and, it follows, that the relationship is linear
Residue analysis	Residues are randomly distributed, indicating that the variance is constant.	The model is well adjusted
Efficiency	Coefficient of determination (R^2) = 0.9981 and maximum efficiency (R_{max}) = 1.00	The obtained value ($R^2 = 0.9981$) demonstrates very high efficiency

Where: MQ_{reg} = mean square due to regression; MQ_r = residual mean square, obtained by ANOVA. The plot of residuals (Fig. 1) indicates that used to indicate how the line can be considered suitable as a mathematical model, and how residuals is randomly distributed indicating not constant variance, the model is ideal [5].

**Figure 1: Plot of residuals**

3.2. Detection and Quantification Limits

3.2.1. Detection limits (LD)

The detection limit was calculated as [5]

$$LD = \bar{X} + t_{(n-1, 1-\alpha)} \cdot s \quad (1)$$

where $\bar{X}$ = average, in concentration, of the blank sample; t = value of t student test; s = standard deviation of blank samples.

Seven blank samples were used to independently determine the detection limit (LD) [5]. The results for each analysis (U and Th) are shown in Table 2.

Table 2: Results obtained for each element

Blank sample	U 238 ($\mu\text{g kg}^{-1}$)	Th 232 ($\mu\text{g kg}^{-1}$)
1	0.066	0.49
2	0.061	0.14
3	0.062	0.09
4	0.065	0.06
5	0.021	0.05
6	0.024	0.05
7	0.014	0.04
Average	0.045	0.13
Standard deviation	0.024	0.16

Giving the following LD for uranium:

$$\text{LD} = 0.045 + t_{(n-1=6, 1-\alpha=99\%)} \times 0.024 = 0.045 + 3.143 \times 0.024 = 0.12 \mu\text{g kg}^{-1}$$

and Thorium:

$$\text{LD} = 0.13 + t_{(n-1=6, 1-\alpha=99\%)} \times 0.16 = 0.13 + 3.143 \times 0.16 = 0.63 \mu\text{g kg}^{-1}$$

3.2.2. Quantification limits (LQ)

The quantification limit (LQ) was calculated as [5]

$$\text{LQ} = \bar{X} + 10s \quad (2)$$

where $\bar{X}$ = average of the blank sample; s = standard deviation of blank samples.

For uranium:

$$\text{LQ} = 0.045 + 10 \times 0.024 = 0.29 \mu\text{g kg}^{-1}$$

and thorium:

$$\text{LQ} = 0.13 + 10 \times 0.16 = 1.7 \mu\text{g kg}^{-1}$$

3.3. Selectivity

The selectivity test was based on the curve generated with tap water and Milli-Q water and analysis of standard reference material. A t-Test was used to assess selectivity. The criteria of the test is that $t_{\text{calculated}} < t_{\text{tabulated}}$. Thus, was obtained $t_{\text{calculated}} = 1.68$ for U and 1.55 to Th, both < 2.23 ($t_{\text{tabulated}}$), concluding that the method is selective and no there is matrix interference.

The results of the analysis in the standard reference material are shown in Table 3.

Table 3: Uranium concentration in certificated standard Reference material

	U^{238} in the analysed aliquot ($\mu\text{g kg}^{-1}$)	Concentration U^{238} (observed value) ($\mu\text{g kg}^{-1}$)	Certified values U^{238} ($\mu\text{g kg}^{-1}$)	Recovery ((observed value/certified value) $\times 100$) (%)
SRM 1640a	8.057	19.834	25.15	79
	8.042	19.799		79
	8.095	19.929		79
Average $\pm$ standard deviation		19.85 ± 0.07		

The uranium in the reference material was not 100% concentrated, so a correction factor was applied based on the concentration indicated by the instrument. For thorium no correction was necessary because the results obtained in synthetic samples ranged from 90 - 100 %. It should be noted that there is no thorium in the standard reference material.

3.4 Results of Samples in Interlaboratory Comparison Program

The results of the samples of the Institute of Radiation Protection and Dosimetry (IRD, Brazil), in the National Intercomparison Program are illustrated Tables 4 and 5. The main objective of this program is to test the methods developed for samples with known amounts of the elements (U and Th) in order to provide a rigorous comparison of the results.

Table 4: Results obtained of uranium in interlaboratory comparison

Samples	Value U (Bq/L)	Reference value of U (Bq/L)	Standard deviation reference value in the program (sd)	Value min.	Value max.
IRD 352	0.941 0.975 0.934	1.010	0.150	0.860	1.160
IRD 394	1.337 1.339 1.267	1.380	0.210	1.170	1.590
IRD 401	0.594 0.590 0.597	0.569	0.085	0.484	0.654

Table 5: Results obtained of thorium in interlaboratory comparison

Samples	Value Th (Bq/L)	Reference value of Th (Bq/L)	Standard deviation reference value (sd)	Value min.	Value max.
IRD 351	0.056 0.053 0.055	0.060	0.009	0.051	0.069
IRD 393	0.091 0.086 0.089	0.090	0.014	0.076	0.104
IRD 400	0.094 0.094 0.095	0.098	0.015	0.083	0.113

The concentrations of uranium and thorium were within the range previously established by the IRD. In the 352 uranium sample, we obtained results equal to 0.941 Bq/L, 0.975 Bq/L and 0.934 Bq/L: all of which are within the maximum and minimum values (illustrated in Table 4). The same applies to samples 394 and 401.

For Th, the range of the 351 sample was equal to 0.056 Bq/L, 0.053 Bq/L and 0.055 Bq/L. Again, all results were within the maximum and minimum limits (as shown in Table 5). The same applies to the sample 393 and 400.

4. CONCLUSIONS

ICP-MS is a fast and effective technique for the determination of U and Th in water samples. The results are consistent with those provided by the National Intercomparison Program, indicating a good performance with the method used. The recovery value found for the reference material showed the accuracy of direct determination using this methodology.

ACKNOWLEDGEMENTS

I thank João Cristiano Ulrich and Jorge Eduardo de Souza Sarkis for academic supervision, and the Coordinator of the Environmental Monitoring Network, Thyara Figueredo France Merlo of the Instituto de Tecnologia e Pesquisa (ITP). The scholarship provided by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). I also thank all those who directly or indirectly contributed to this work.

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