

DETERMINATION OF URANIUM IN TREE BARK SAMPLES BY EPITHERMAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

In this study uranium (U) concentrations were determined in certified reference materials (CRMs) and in tree bark samples collected in “Cidade Universitária Armando de Salles Oliveira” (CUASO) USP, São Paulo. The barks were collected from different species namely *Poincianella pluviosa* and *Tipuana tipu*. These bark samples were cleaned, dried, grated and milled for the analyses by epithermal neutron activation analysis method (ENAA). This method consists on irradiating samples and U standard in IEA-R1 nuclear reactor with thermal neutron flux of $1.9 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ during 40 to 60 seconds depending on the samples matrices. The samples and standard were measured by gamma ray spectroscopy. U was identified by the peak of 74.66 keV of ^{239}U with half life of 23.47 minutes. Concentration of U was calculated by comparative method. For analytical quality control of U results, certified reference materials were analysed. Results obtained for CRMs presented good precision and accuracy, with $|\text{Z score}| \leq 0.39$. Uranium concentrations in tree barks varied from 83.1 to 627.6 ng g^{-1} and the relative standard deviations of these results ranged from 1.8 to 10%.

1. INTRODUCTION

The U is a metallic and radioactive chemical element that is naturally distributed in the ground with concentrations between 0.1 and 20 mg kg^{-1} [1]. This element is found in different concentrations in water, air and foods. The increasing application of U in nuclear industry, agriculture and in nuclear weapons fabrication indicates that this element has been systematically extracted from nature and then deposited in the environment, which makes transference to water, plants and aliments possible.

It is well known that U is a toxic element for human beings and consequently it represents a significant hazard to human health [2]. By considering all the damages that this element can cause to organism it is of great importance to determine U concentration mainly in the environmental samples. In general, U is present in biological and environmental samples at very low concentrations. This fact becomes necessary to evaluate the quality of the results obtained for this element in order to get reliable data.

There are several analytical methodologies used for U determination. The most used ones are inductively coupled plasma mass spectrometry (ICP-MS) [3-5], X-ray fluorescence spectrometry (XRFS) [6], flame atomic absorption spectrometry (FAAS), electrothermal

atomic absorption spectrometry (ET AAS), optical emission spectrometry with an inductively coupled plasma source (ICP OES), neutron activation analysis (NAA) [7,8], delayed neutron activation analysis (DNAA) [9], liquid scintillation counting (LSC) [10,11], gamma spectroscopy [12] and alpha spectroscopy [13,14]. Among these analytical methods for U quantification, neutron activation analysis was selected to be used in this study. This method was chosen based on its simplicity, precision, fastness, availability and easy access to use it.

This research consisted on U determination in tree barks used as environmental pollution biomonitor and certified reference materials by using short irradiation of ENAA method.

2. EXPERIMENTAL

2.1. Tree Bark Sample Collection

Tree bark samples of two different arboreal species, namely *Tipuana tipu* (Tipuana) and *Poincianella pluviosa* (Sibipiruna), were collected at the Cidade Universitária Armando de Salles Oliveira (CUASO) of University of São Paulo, located in São Paulo city at Butantã district.

The total number of collected tree bark samples were eight, and they were obtained in different sites of CUASO during the period January and February, 2017. The sampling points were randomly chosen considering only where the tree species were found. Bark samples were removed, by using a stainless steel knife, from trees at about 1.5 m from the topsoil and they were placed in paper bags.

2.1.1. Preparation of Tree Bark Samples for the Analyses

Firstly, tree bark samples were dried in an oven (FANEM mod. 320-SE) with forced air circulation at 40 °C for about 48 hours. In next step, the barks were cleaned using a tooth brush with nylon bristles in order to remove dust and extraneous materials. Then 3 mm of the external layer of tree barks were removed by using a titanium grater. To obtain a powder form, the sample was milled for homogenization by using a Fritsch “Analysette 3 Pulverisette 0” micro mill. After this process this powder was placed in plastic vials and stored in a desiccator.

2.2. Certified Reference Materials

Certified reference materials (CRMs) are used for ensuring metrological traceability and they are also used to evaluate accuracy and precision of the results. The reference materials IAEA 140/TM Trace elements and methylmercury in seaweed (*Fucus* sp.), NIST - 1575 Pine needles, NIST - 1632d Trace elements in coal (Bituminous), NIST - 1633b Constituent elements in coal fly ash, INCT - MODAS-3 Herring Tissue, IAEA - Soil-7 Trace elements in soil and IAEA - RLA 2/014 Trace elements in volcanic ashes were analysed in this study.

To calculate U concentrations on dry weight basis, the humidity of CRMs were determined. This determination consisted on drying an aliquot of each material at temperature of 85 °C for biological materials and 110 °C for geological materials both for 48 hours or until to obtain constant mass. The percentage of humidity obtained is presented in Table 1.

Table 1: Percentage of humidity determined in the certified reference materials

Certified Reference Materials	Humidity (%)
IAEA-140/TM Seaweed	4.7
NIST-1632d Trace Elements in Coal	5.6
NIST-1633b Coal Fly Ash	1.3
IAEA-RLA2/014 Volcanic Ashes	0.3
IAEA-SOIL-7 Trace Elements in Soil	11.2
NIST - 1575 Pine Needles	1.1
INCT - M3 Herring Tissue	1.4

2.3. Preparation of Synthetic Standard of Uranium

The diluted U standard solution was prepared by using a certified standard solution from Spex Certiprep Chemical (USA) with concentration of $1003 \pm 3 \text{ mg L}^{-1}$. The diluted standard solution was prepared using MILLI-Q water and this solution was stored at 8 °C, in a refrigerator. Before using it, this solution was kept at room temperature in order to achieve thermal equilibrium.

Fifty microliters of diluted U standard solution were pipetted onto sheets of Whatman *n*° 40 filter paper with the dimensions of 1.5 cm × 6 cm. This synthetic standard was kept in a desiccator in order to dry the pipetted aliquot. After drying, these sheets were folded and placed into polyethylene involucres. Concentration of pipetted solution was of $200.51 \mu\text{g mL}^{-1}$ and U mass irradiated was $10.02 \mu\text{g}$.

2.4. Procedure for Epithermal Neutron Analysis

Aliquots of each sample were weighed in polyethylene involucres. A mass of 100 mg in the case of geological material and 200 mg for biological material was weighed. For irradiating, a sample and U synthetic standard were placed in a cadmium (Cd) capsule and that was placed inside a polyethylene device (rabbit).

The irradiation times varied from 15 and 40 seconds depending on sample. They were sent for irradiation using pneumatic station of the IEA-R1 reactor of IPEN - CNEN/SP. The thermal neutron flux used was of $1.9 \times 10^{12} \text{ n cm}^{-2}\text{s}^{-1}$. After irradiation, the sample and the standard were mounted in a stainless steel planchet for counting. The induced gamma activities were measured using a high-purity Ge detector (CANBERRA), model GC2018,

connected to DSA 1000 digital spectrum analyser (CANBERRA). The resolution of the system (FWHM) were 1.05 keV for 121.97 keV peak of the ^{57}Co and of 1.89 keV for 1332 keV gamma-ray of ^{60}Co . A chronometer was used to record the final irradiation time and count start and end times. Spectral data acquisition and its processing were carried out using Genie 2000 software, version 3.1 (CANBERRA). Counting times of 500 seconds were used for the samples and standard. Uranium was identified by gamma-rays of 74.66 keV of ^{239}U with a half life of 23.47 minutes. The U concentration was calculated by comparative method according to De Soete et al. [15].

2.5. Treatment of Data

Uranium results obtained in this study were evaluated using basic statistic calculating arithmetic mean (M), standard deviation (SD), relative standard deviation (RSD) and relative errors (RE). Moreover, the standardized difference or Z score value was calculated to evaluate accuracy of the results. The Z score was calculated according to Konieska and Namieśnik [16] using equation 1.

$$Z = \frac{x_{lab} - x_{ref}}{\sqrt{DP^2 - u_{ref}^2}}, \quad (1)$$

where x_{lab} is the obtained value, x_{ref} is the certified value, u_{ref} is the combined uncertainty of the certified value and DP is the standard deviation of the results obtained.

The criteria of Z score values are [16]:

- If $|Z| \leq 2$ the result is considered satisfactory;
- If $2 < |Z| < 3$ the result is considered uncertain;
- If $|Z| \geq 3$ the result is considered unsatisfactory.

The detection and quantification limits were calculated using equations 2 and 3, respectively, according to Currie [17].

$$LDT = 3.29 \cdot \frac{BG^{1/2}}{LT} \quad (2)$$

$$LQT = 10 \cdot \frac{BG^{1/2}}{LT} \quad (3)$$

where LDT and LQT are count rates for the minimum detectable and quantifiable concentrations, respectively; BG is counting rate of background, which corresponds to area under the peak and LT is the counting time. Once the values LDT and LQT have been calculated, the limits in terms of concentrations were obtained using comparative method.

3. RESULTS AND DISCUSSION

3.1. Uranium Results in Certified Reference Materials

In Table 2, U concentrations obtained in CRMs are presented. In this Table, the detection limits values and certified values are also presented. Uranium concentrations obtained in the analyses of CRMs indicate good agreement with the certified values. The relative errors obtained in these results varied from 0.1 to 3.1% and $|Z \text{ score}|$ were lower than 0.39. In the CRMs 1575 Pine Needles and M3 Herring Tissue CRMs U was not detected using short irradiation of ENAA due to its low concentration in these two materials. As can be seen in Table 2 the U concentrations in these materials are lower than their respective detection limits values.

3.2. Uranium Determination in Tree Bark Samples

The U concentrations obtained of tree bark samples are shown in Table 3. In this Table, the mean of concentrations with standard deviation, relative standard deviation and values of detection limits and quantification limits are presented.

Table 3: Uranium concentrations and values of detection and quantification limits in tree barks samples

Sample Codes	$M \pm SD^a(n)^b$ ($ng\ g^{-1}$)	RSD ^c (%)	Detection Limits ($ng\ g^{-1}$)	Quantification Limits ($ng\ g^{-1}$)
NC1	103.9 \pm 7.9 (3)	7.6	30.8	93.8
NC2	83.1 \pm 8.3 (4)	10.0	37.2	113.3
NC3	132.9 \pm 2.4 (3)	1.8	93.0	282.9
NC4	97.2 \pm 7.0 (3)	7.2	37.1	112.8
NC5	213 \pm 19 (3)	9.0	44.2	134.7
NC6	574 \pm 22 (3)	3.8	79.9	243.4
NC7	205.9 \pm 4.3 (4)	2.1	51.8	157.7
NC8	627.6 \pm 22.6 (3)	3.6	122.5	371.9

a. Arithmetic mean and standard deviation. b. Number of determinations; c. Relative standard deviation.

Uranium concentrations obtained in tree bark samples show precise results with relative standard deviations varying from 1.8 to 10 %. The reproducibility of these results also indicates the homogeneity of prepared bark sample in relation to U concentration. The detection limits presented in Table 3 indicate the high sensitivity of the ENAA procedure

for U determined in tree barks. The U concentrations obtained in the tree barks collected at CUASO of São Paulo University varied from 83.1 to 628 $ng\ g^{-1}$ and the origin of this element in tree barks can be attributed to suspension of soil dust deposited by the wind.

Table 2: Uranium concentrations determined in certified reference materials

Certified Reference Materials	Certified Value (<i>ng g⁻¹</i>)	M ± SD ^a (n) ^b (<i>ng g⁻¹</i>)	RSD ^c (%)	RE ^d (%)	Z - score	Detection Limits (<i>ng g⁻¹</i>)	Quantification Limits (<i>ng g⁻¹</i>)
IAEA-140/TM Seaweed	730(467-813)	729±77 (4)	10.5	0.1	-0.01	217.6	662.0
NIST-1632d Trace Elements in Coal	517±12	533±71 (5)	13.4	3.1	0.22	115.2	349.6
NIST-1633b Coal Fly Ash	8790±360	8658±876 (7)	10.1	1.5	-0.15	328.6	985.7
IAEA-RLA2/014 Volcanic Ashes	8500±600	8741±543 (5)	6.2	2.8	0.39	336.3	1047.7
IAEA-SOIL-7 Trace Elements in Soil	2600(2200-3300)	2585±153 (4)	6.0	0.6	-0.04	698.9	1637.9
NIST - 1575 Pine Needles	20±4	ND ^e	-	-	-	252.4	766.8
INCT - M3 Herring Tissue	75.2±4.1	ND ^e	-	-	-	390.4	1186.8

a. Arithmetic mean and standard deviation. b. Number of determinations; c. Relative standard deviation. d. Relative error. e. Not detected.

4. CONCLUSIONS

Results obtained in this study demonstrated that procedure of ENAA using short irradiation can be applied satisfactorily in U determination in environmental samples of tree barks. The results obtained in the analyses of certified reference materials presented good precision and accuracy. The detection limits depend on the composition of the samples and in the case of tree barks these were very low (lower than $122.5 \mu\text{g g}^{-1}$).

ACKNOWLEDGMENTS

The authors would like to thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. The author N. P. de Lima is grateful for a scholarship from the CNPq.

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