Intercomparison of thorium and uranium results obtained by X-ray energy dispersive spectrometry and neutron activation analysis

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ABSTRACT

The objective of this work is to evaluate the performance of the X-Ray Energy Dispersive Spectrometry as an additional analytical support to the development of the chemical process of Uranium and Thorium separation and concentration by liquid-liquid extraction technique. Results obtained from the Neutron Activation Analysis by Instrumental and Fission Delayed Neutrons methods were used to establish the intercomparison. Uranium and thorium were extracted from monazite sulphuric liquor. The analytical techniques were applied on both organic and aqueous samples.
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INTRODUCTION

Thorium (Th) and Uranium (U) have a strategic role in the nuclear power generation. At the nuclear point of view they belong to a material class named fertile. Monazite, a rare-earth mineral phosphate, is one of the main sources of thorium element in the world. Uranium has been also found associated to rare-earth elements but in a very small amount compared to thorium[1,2]. The process, whose procedures are referred in this work and from which samples are originated, aims at recovering thorium and uranium from the liquor of monazite leaching supplied by Nuclear Industries of Brazil (INB/Caldas-MG).

The studies for recovering thorium and uranium elements were led by the liquid-liquid extraction technique[3]. This process consists of a selective transference on the metallic species of interest from the aqueous phase to an immiscible organic phase. The last one is an extractant that is diluted in an appropriate solvent. The transference process is achieved by putting the phases in contact followed by separation of the same ones[4]. Aqueous and organic samples are generated. In order to follow the process in a way to keep up with all changes over variables it is important to have an efficient analysis support that is able to give results on time. On the uranium determination by using Neutron Activation technique, these requirements are fulfilled but that is not the case for thorium that demands a long time to be analysed. Aiming at overcoming this problem X-Ray Fluorescence Spectrometry was then introduced as an alternative technique. It has the advantages of being able to give results on time and also offering uranium and thorium determination together. This initiative has then given the opportunity to compare results from each technique used in this work.

NEUTRON ACTIVATION ANALYSIS

Neutron Activation Analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples with accuracy and precision[5,6]. NAA is generally recognized as the 'reference method' of choice when new procedures are being developed or when other methods yield results do not agree. Methods of chemical analysis are based on the behavior of electrons from the outer levels in the atom. Activation differs from most other methods because it is based on the properties of nuclei. That means it is a purely elementary analysis method.

Basically, the activation process involves exposure to a source of neutrons, that is the most common way of activation, usually using nuclear reactors. CDTN(Nuclear Technology Development Center), sponsored by CNEN(Brazilian Commission for Nuclear Energy), has available a TRIGA Mark I IPR-R1 research reactor for neutron irradiation.

Analytical method

In this work, Neutron Activation Analysis technique was applied by using two methods consisted in analysing the sample without any previous chemical procedure: the Instrumental method (INAA) to determine thorium and Delayed Fission Neutron Activation (DFNA) method to determine uranium[7,8]. In both methods, the procedure for preparing samples is to pipette the aqueous and organic samples to polyethylene vials suitable for irradiation. Also, standards of the chemical elements were analysed together and the concentration of thorium and uranium were calculated by linear regression.

To determine ^{232}Th (cross-section 7.3 barns) an exposure to the average thermal neutron flux for 2 hours in the rotary rack was enough to produce ^{233}Th, (22.4 - minute half-life and main γ-rays 86.6, 162.3, 169.3, 459.2 keV; reaction (n,)). After β-particle emission, ^{233}Pa, (27 - day half-life and main γ-rays of 299.9(15%), 311.8(100%), 340.3(4%) keV), was produced. Due to these nuclear characteristics, ^{232}Th was determined by means of ^{233}Pa, long half-life[5,9]. The measurements, by gamma spectroscopy, were carried out by ^{233}Pa after the shorter and middle half-life radionuclides decay about 10 days. The gamma spectrometry system consisted in a coaxial HPGe detector with 15% relative efficiency and 1.66 keV FWHM resolution at 1,332.5 keV γ-rays for ^{60}Co. It was used a specific software for gamma spectrum acquisition.

Concerning the determination of uranium, the DFNA method applied is specific to uranium analysis when the samples are irradiated with thermal neutrons. It is based on a short irradiation followed by measurement of the delayed neutrons. Usually, an irradiation time of 60 seconds, decay time of 30 seconds and measurement time of 60 seconds are used. A pneumatic transfer system is used for irradiation and the delayed neutrons are counted in a device comprising ^{10}BF$_3$ detectors in a moderator of paraffin[8]. The whole procedure is completely automatic with sample changer, pneumatic transfer system, measurement electronics and computer.

Principles of energy dispersive spectrometer

The instrumental apparatus used in our laboratory is a configuration of the Si(Li) X-Ray Spectrometry System that incorporates the concept of excitement by radioisotope. It is a KEVEX system, SIGMAX 9050 model, with a built-in ^{241}Am source as the primary photons beam.

Atoms can be taken to a special state of excitement as a consequence of the interaction with photons which have enough energy to pull electrons off the more internal occupation layers. In this condition, the immediate return to the fundamental state results in X-ray emission. The origin of these radiation emissions is a result of a decay process characterised by internal electronic transitions from which X-ray spectra, with discrete values to the wavelength, are produced. According to the chemical orbital theory, these spectra reflect the discrete nature of the energy values that are involved in the electronic transitions.

These are the fundamental aspects of the X-ray Spectrometry that has in the Si(Li) solid-state device the alternative version to classify photons according to the energy: the amplitude of the electrical pulse produced inside the device has its height proportional to the photon energy. It is called an X-Ray Energy Dispersive Spectrometry (EDS)[10,11].

Analytical method

The quantitative X-Ray Spectrometer is based on

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TABLE 1 : Uranium and thorium determinations-aqueous samples

Code	Thorium (g.L⁻¹)			Uranium (g.L⁻¹)		
	NAA	EDS	NAA / EDS	NAA	EDS	NAA / EDS
01	< 0.001	< 0.03	-	< 0.001	< 0.03	-
02	< 0.001	< 0.03	-	< 0.001	< 0.03	-
03	0.90 ± 0.01	0.80 ± 0.04	1.13	0.12 ± 0.01	0.13 ± 0.01	0.94
04	4.22 ± 0.04	3.5 ± 0.1	1.21	0.14 ± 0.01	0.17 ± 0.01	0.84
05	8.6 ± 0.1	7.5 ± 0.3	1.14	0.29 ± 0.01	0.34 ± 0.01	0.86
06	20.5 ± 0.2	21 ± 1	1.02	0.61 ± 0.03	0.65 ± 0.02	0.93
07	29.6 ± 0.3	28 ± 1	1.04	0.62 ± 0.03	0.58 ± 0.02	1.07
08	30.8 ± 0.3	29 ± 1	1.07	0.62 ± 0.03	0.60 ± 0.02	1.04
09	31.9 ± 0.3	30 ± 1	1.07	0.64 ± 0.03	0.64 ± 0.02	1.01
10	33.1 ± 0.3	29 ± 1	1.12	0.87 ± 0.04	0.94 ± 0.04	0.92

TABLE 2 : Uranium and thorium determination-organic samples

Code	Thorium (g.L⁻¹)			Uranium (g.L⁻¹)		
	NAA	EDS	NAA/EDS	NAA	EDS	NAA/EDS
01	< 0.001	< 0.003	-	0.016 ± 0.002	0.02 ± 0.01	0.76
02	< 0.001	< 0.003	-	0.06 ± 0.01	0.06 ± 0.03	1.07
03	0.025 ± 0.002	0.013 ± 0.005	1.92	0.117 ± 0.005	0.10 ± 0.01	1.17
04	0.050 ± 0.004	0.07 ± 0.01	0.70	0.121 ± 0.005	0.11 ± 0.01	1.10
05	0.10 ± 0.01	0.10 ± 0.01	1.00	0.13 ± 0.01	0.13 ± 0.01	1.02
06	1.31 ± 0.02	1.14 ± 0.05	1.15	0.17 ± 0.01	0.14 ± 0.01	1.19
07	3.2 ± 0.01	2.9 ± 0.1	1.11	0.17 ± 0.01	0.10 ± 0.01	1.74
08	4.3 ± 0.1	4.0 ± 0.2	1.08	0.21 ± 0.01	0.20 ± 0.01	1.04
09	5.7 ± 0.1	5.0 ± 0.2	1.14	0.22 ± 0.01	0.21 ± 0.01	1.03
10	5.7 ± 0.1	5.5 ± 0.2	1.04	0.24 ± 0.01	0.22 ± 0.01	1.11

the proportionality between the characteristic X-ray intensity produced in the sample and the concentration of the correspondent chemical element. The X-ray spectrum from a material being analysed is a composition of characteristic spectra of the several components presents in the sample. The main problem is then to determine the real value of these intensities by considering the matrix influences as absorption, secondary fluorescence and spectral interferences.

An initial estimate of the values of these intensities can be obtained by using the Square Minimum Method[12] in which the original spectrum can be synthesised from components that are the characteristic spectra of elementary standards. The application of this method requires a collection of elementary standards sufficient to cover all elements present in the sample with peaks in the spectral interest region. It also has to consider the two types of sample representation: aqueous and powder tablets.

X-rays are absorbed in the path from the point where they are generated until they escape from the sample surface. This fact can introduce serious displacement of a linear relation between intensity and concentration. Due to inherent proprieties of the primary source of excitement the absorption effects are treated in an experimental way according to the procedures described in the Emission-Transmission Method[13,14]. Based on the measurement of the sample transmittance to a particular X-ray energy-normally the one associated to the strongest peak-by comparison with a standard, the method sets a correction factor for the chemical element being analysed.

Sample preparation

Aqueous samples are represented by an 1ml-sized aliquot. Surface tension effects can be overcome by using a rigid disc made of an X-ray transparent material installed in direct contact with the surface. A more elaborated procedure is required by organic samples. The 1mL-sized aliquot is deposited on a piece of cotton and burned inside a porcelain crucible at 800ºC for an hour. The residue is removed and the mass is completed up to 200 mg. After that, the material is compacted in order to form a cylindrical powder tablet. For both types of preparation, the measurement time on the photons primary source is 800s.

RESULTS AND DISCUSSION

Ten samples were selected to evaluate the EDS performance compared with the NAA technique. The results shown in Tables 1 and 2 point out that below the detection limits presented by the techniques (0.001 g.L⁻¹ for Th and U, NAA; 0.03 g.L⁻¹ for Th and U in aqueous samples-0.003 g.L⁻¹ for Th and U in organic samples, EDS), the values are in good agreement.

The main concern here was the ratio NAA to EDS results that is more appropriate to decide about the X-Ray Analysis performance. Observing the columns ratio NAA/EDS it is possible to verify the following, excluding the values below the detection limits: (i) for Th (aqueous and organic samples) and U (aqueous

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samples), 88% of the samples presented results below 15% of variability; (ii) for U in organic samples, 60% of the samples presented results below 15% of variability.

CONCLUSIONS

The EDS technique, applied as a support for this process, proved to be efficient due to a quick answer even presenting higher detection limit than the NAA. The variability of 15% between the EDS and NAA results is suitable for the purpose of this research.

In this work, it is concluded that both techniques have relevant role in the chemical processes: EDS to follow and guide the steps of the process and NAA to refine the results. It is suggested to keep both analytical procedures to complete the chemical information to the samples.

Approximately 80% of the samples that present EDS values higher than the results from the NAA should be more investigated.

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