URANIUM AND THORIUM DETERMINATION IN SANTA QUITÉRIA LIQUOR
BY ICP-OES ANALYSIS

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ABSTRACT

The mineral source of Itataia located in Santa Quitéria (Ceará / Brazil) is a phosphorus-uraniferous one, where uranium occurs in collophanite (fluorapatite) form. Phosphate minerals of the apatite family make possible the uses of uranium as a byproduct. The sulfuric leaching of the phosphate rock in order to obtain phosphoric acid also permits uranium recovery. Thus, the liquor coming from the leaching contains high levels of phosphoric acid as well as elements like Mg, Fe, U, Zr, Th and some rare earths in significative concentrations. The direct determination of U and Th content of this liquor is essential to a rapid response in the uranium separation and purification together process by solvent extraction, aiming its use for commercial purposes, as nuclear industry fuel. In this study U and Th were determined by Inductively Coupled Plasma Spectrometry (ICP-OES) in several samples of liquor, in high concentrations of H₃PO₄ in environment. Several ratios of U/Th and H₃PO₄ concentrations were studied, in order to find the optimal conditions for the direct determination of U and Th, without need to prior separation.

1. INTRODUCTION

The source of Itataia located in Santa Quitéria (Ceará, Brazil) is a phosphorus-uraniferous, occurring in the form of colofanito (fluorapatite), representing 3.5% and 46% of Brazilian reserves of phosphorus and uranium respectively. The concentration of uranium varies from 50-200 mg kg⁻¹ [1]. These data is relevant, because indicate that this deposit is the largest reserve of uranium in Brazil [2]. Phosphoric acid is obtained by leaching of sulfuric rock phosphate. This process also enables the recovery of uranium. Thus, the leaching liquor has come from the addition of high levels of phosphoric acid, elements such as Mg, Fe, U, Zr, Th and some rare earth in appreciable concentrations.

The enormous quantity of mineral phosphate in the world enables the use of uranium as a byproduct and, in this sense, the recovery of the element contained in phosphate rocks is the subject of many study, because there it is more associated with uranium in phosphate mineral elements. The production of wet phosphoric acid, obtained by leaching rock phosphate with
inorganic acids (particularly the sulfuric), enables the recovery of uranium by liquid-liquid extraction [1].

The direct determination of U and Th content of this liquor is crucial for a rapid monitoring of the separation and purification of uranium. This element is the raw material to start manufacturing the fuel element, employed mainly as a source of energy in nuclear reactors to generation of electricity.

In this study, U and Th were studied by emission spectrometry in plasma (ICP-OES) in the midst in high concentration of phosphoric acid. One of the main reason for merger U and Th analysis is find out the ideal conditions for the direct determination of these elements without the need for prior separation between them.

2. MATERIALS

An emission spectrometry in the Argon Inductively Coupled Plasma (ICP-OES) Perkin Elmer, model Optima 2100 DV was used for determinations of uranium and thorium.

Stock solutions of uranium (100 ppm) and thorium (100 ppm) were prepared in HNO$_3$ 0.1mol L$^{-1}$ from standard solutions of 1000ppm. Analytical curves were prepared for uranium and thorium in HNO$_3$ 0.1mol L$^{-1}$ and H$_3$PO$_4$ 0.7mol L$^{-1}$. Stock solutions and their dilutions were prepared by mass in a Bel 500 semi-analytical balance with three decimal places.

The water used was doubly distilled and all reagents were of analytical grade.

3. EXPERIMENTAL PROCEDURE

Solutions of phosphoric acid were prepared by dilution mass balance in semi-analytical three places in the following concentrations: 0.07M, 0.14M, 0.7M and 1.4M. These solutions were analysed in ICP-OES operating conditions (Table 1) and the wavelengths of 409.014nm and 401.913nm respectively in curves of uranium and thorium.
Table 1. Operating conditions of ICP-OES

| Power of Plasma                          | 1300 W |
| RF Generator                             | 40 MHz |
| Vista Axial - Position (mm)              | Horizontal: 0  
|                                         | Vertical: 15  |
| Nebulizer                                | Glass, Meinhard |
| Gas Flow (L min⁻¹)                       | 15 |
| Plasma                                   | 0,2 |
| Auxiliar                                 | 0,8 |
| Aspiration (ml min⁻¹)                    | 1,5 |
| Integration Time (s)                     | 10 |
| Number of Replicates                     | 3 |

Solutions of phosphoric acid were then prepared in the same concentrations of the test before adding 1.0ppm uranium. This experiment was repeated by adding from 5.0ppm to 1.0ppm instead of uranium. All solutions were read in ICP-OES analytical curves prepared in the range of 0.1 to 10ppm uranium in 0.1M nitric acid medium and the wavelengths of 409.014nm.

For analysis of thorium, solutions were prepared by mass of phosphoric acid in the same concentrations of the first test of adding 1.0ppm thorium. This experiment was repeated for this experiment instead of adding 5.0ppm to 1.0ppm thorium.

All solutions were read in ICP-OES calibration curves prepared in the range of 0.1 to 10ppm thorium in 0.1M nitric acid medium and a wavelength of 401.913nm.

The concentrations of phosphoric acid sulfuric liquor were around 5 to 7 mol L⁻¹[1]. Samples of the liquor were diluted 10 times to be read in ICP-OES, due to the high uranium content, acidity and viscosity. Analytical curves were prepared for both of thorium as for uranium in 0.7 mol L⁻¹ phosphoric acid.

Taking into consideration that the average concentration of uranium is 1830ppm, and average concentration of thorium is 182ppm liquor in the Santa Quitéria [1], ie the concentration ratio of U/Th is about 10 times, and the concentration of approximately phosphoric acid of 5 to 7 mol L⁻¹, were prepared in 0.7 mol L⁻¹ phosphoric acid solutions at various grounds of uranium / thorium: 100 times, 75 times, 50 times, 25 times, 10 times, 5 times, and 1:1.
4. RESULTS AND DISCUSSIONS

The wavelengths of 409.014 nm for the determination of uranium and 401.913 nm for thorium [3,4], were chosen because they did not showed interference from iron in the liquor in concentrations of about 12000 ppm [1].

The solutions of phosphoric acid in concentrations 0.07 mol L\(^{-1}\), 0.14 mol L\(^{-1}\), 0.7 mol L\(^{-1}\) and 1.4 mol L\(^{-1}\) were used as blank in the determination of uranium and thorium, both at concentrations of 1.0 ppm and 5.0 ppm.

In tests involving uranium in the presence of phosphoric acid, was observed an increase in the concentration of uranium (Figures 1 and 2). For the previous report under the same conditions, it was observed a decrease in the concentration of thorium (Figures 3 and 4).

![Figure 1. Determination of 1.0 ppm uranium in different concentrations of H3PO4. (409.014 nm)](image-url)
Figure 2. Determination of 5.0ppm uranium in different concentrations of $\text{H}_3\text{PO}_4$. ($409.014\text{nm}$)

Figure 3. Determination of 1.0ppm thorium in different concentrations from $\text{H}_3\text{PO}_4$. ($401.913\text{nm}$)

Figure 4. Determination of 5.0ppm thorium in different concentrations from $\text{H}_3\text{PO}_4$. ($401.913\text{nm}$)

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Once the levels of phosphoric acid in samples of bleach was well known, the interference of phosphoric acid in uranium and thorium measurements could be corrected with the analytical curves prepared by using phosphoric acid in the same concentrations of liquor, thereby eliminating the matrix effect.

For the tests involving the mixing uranium and thorium, with variations in concentration of the ratios U / Th and 0.7mol L$^{-1}$ phosphoric acid, it was observed the following considerations:

In determinations of thorium, the increase of the ratio of concentrations U / Th, caused a significant increase in the concentration of thorium (Figure 5). However, this increase in concentration measurements occurred in a linear way in way that it increased the concentration ratio of U/Th (Figure 6). Once the concentration of uranium was well know, it was possible to establish a correction factor for the concentration values of thorium [3].

\[ y = 1.4692x - 1.4594 \]
\[ R^2 = 0.9985 \]

**Figure 5. Variation of Th concentrations with increasing concentration of uranium (401.913nm)**

\[ y = 1.4692x - 1.4594 \]
\[ R^2 = 0.9985 \]

**Figure 6. Interference ratio of the increase in U/Th in the Th concentration in ppm (401.913nm)**

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We also observed that for ratio of concentrations U/Th of less than 10 times, the interference of uranium concentration in the reading of the report can be considered negligible (Figure 5). For ratio of concentrations U/Th than 10 times, you can reduce the interference of uranium through the addition pattern of thorium, thereby decreasing the concentration ratio of U/Th to values less than 10 times [3].

In determinations of uranium, the increasing of the concentration ratio of U/Th decreases the thorium interference in the concentration of the uranium values from negligible to 10 times higher grounds (Figure 7). For ratio less than 10 times, you can reduce the interference by the addition of thorium to uranium standard, bringing the concentration ratio of U/Th to values greater than 10 times.

![Figure 7. Interference ratio of the increase in U/Th in the sign of U in ppm (409.014nm)](image)

5. CONCLUSIONS

The results show that ICP-OES technique analysis can be used for U and Th determination in sulfuric leaching from phosphate rocks without any previous separation between U and Th. For the U analysis, the U/Th ratio must be greater than 10; for Th analysis, less than 10.

If the samples do not have these conditions, the U determination can be performed using the standard addition technique and Th determination using either standard addition technique or, once known the U concentration, providing a correction factor (Figure 6).
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REFERENCES


