

## **$^{230}\text{Th}$ , $^{232}\text{Th}$ AND $^{238}\text{U}$ DETERMINATIONS IN PHOSPHORIC ACID FERTILIZER AND PROCESS PRODUCTS BY ICP-MS**

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### **ABSTRACT**

Through processing of Santa Quitéria-CE mine phosphate rock, Brazil has established a project for production of phosphoric acid fertilizer and uranium as a by-product. Under leaching conditions of phosphate rock with sulfuric acid, which is the common route for preparing phosphoric acid fertilizer, a large part of uranium, thorium and their decay products naturally present in the rock are solubilized. In order to assess the contamination potential in phosphoric acid and others process products, this paper describes a previous precipitation and direct methods for routine analysis of thorium and uranium isotopes by ICP-MS. In all samples,  $^{230}\text{Th}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  were directly determined after dilution, except  $^{230}\text{Th}$  in phosphoric acid loaded with uranium sample, which to overcome equipment contamination effect, was determined after its separation by oxalate precipitation using lanthanum as a carrier. The results obtained by the proposed method by ICP-MS, were in good agreement when compared to alpha spectrometry for  $^{230}\text{Th}$ , and ICP-OES and spectrophotometry with arsenazo III for elementary uranium and thorium determinations.

*Keywords:* Inductively coupled plasma mass spectrometry;  $^{230}\text{Th}$ ;  $^{232}\text{Th}$ ;  $^{238}\text{U}$ ; phosphoric acid fertilizer

### **1. INTRODUCTION**

In order to increase soil productivity, modern agriculture is dependent on phosphate rock as a source of phosphorus in addition to other added fertilizers based on nitrogen and potassium. The production process of phosphoric acid, which is the starting input in the production of fertilizers and other industrial applications, consists in the dissolution of phosphate rock with sulfuric acid, resulting in phosphoric acid and calcium sulphate, or phosphogypsum, as waste.

It is estimated that 82% of the phosphate produced is employed in the fertilizer industry where it is converted predominantly into DAP (diammonium phosphate), MAP (monoammonium phosphate) and TSP (triple superphosphate). The remaining 18% is directed to other industrial applications such as the manufacture of detergents, water treatment chemicals, bread leavening agents, animal feed supplement and non-alcoholic beverages (soft drinks) [1].

According to the U.S. Geological Survey Yearbook 2015, the largest reserves of phosphate rocks are located in the following countries, in million metric tons (mmt): Morocco and

Western Sahara - 50,000; China - 3,700; Algeria - 2,200; Syria - 1,800; South Africa - 1,500; Jordan - 1300, Russia - 1,300 and the United States - 1,100. The Brazilian reserve amounts to 270 mmt [2].

The world's resources of uranium in phosphate rocks are estimated at  $9 \times 10^6$  metric tons, with average content ranging from 0.005 to 0.02% of  $U_3O_8$ . In comparison, some commercial Canadian rocks present content levels above 15%; while in India content levels of 0.06% (Jaduguda Mine) and 0.3% (AndhraPradesh Mine) are observed in processed ores. Since the fuel cost is a minor component of the total cost of nuclear electricity, countries that seek energy self-sufficiency find it imperative to use their domestic uranium resources, even with low uranium concentration deposits [3].

The main uranium source known in Brazil today, located in Santa Quitéria-CE, is associated to phosphate rock, occurring in fluorapatite form, with its reserves amounting to 14 million tons of  $P_2O_5$  and 142 million tons of  $U_3O_8$ . The average content of the mined ore is in the order of 11% of  $P_2O_5$  and 0.09% of  $U_3O_8$  [4]. The main steps of the process developed for the utilization of phosphorus and uranium from Santa Quitéria involve ore treatment phases such as flotation (in order to concentrate uranium-bearing apatite), phosphate concentrate leaching with sulfuric acid to produce phosphoric acid containing uranium, and solvent extraction of uranium contained in the phosphoric acid. The solvent used for extraction of uranium from the aqueous phase consists of two extractants, Di-(2-ethylhexyl) Phosphoric Acid (DEHPA) and Trioctylphosphine oxide (TOPO), dissolved in aliphatic diluent.

After uranium removal, thorium isotopes still remain in the phosphoric acid. In the case of Santa Quitéria, the activities of  $^{230}Th$  - a daughter of  $^{238}U$  - range between 15 and 20 Bq/g while those of  $^{232}Th$  are found from 0.3 to 0.5 Bq/g. Thus, this product must be submitted to purification processes, especially with its commercial aim as a supplement in the manufacture of foodstuffs for human and animal consumption and soft drinks.

Regarding the chemical controls of phosphoric acid production and purification processes of by-products, several methods on the determination of uranium and thorium are reported in the literature. These include, for example, gamma ray spectrometry [5 and 6], neutron activation analysis [7 and 8], spectrophotometric methods [9 and 10] and inductively coupled plasma optical emission spectrometry (ICP-OES) [11 and 12]. Due to its high sensitivity, alpha Spectrometry is one of the most employed techniques of actinide isotopes determination. However, it presents the disadvantage of requiring a large counting time to achieve good statistics and, consequently a lower associated uncertainty. However, with inductively coupled plasma mass spectrometry, ICP-MS, technique becoming relatively common in many analytical laboratories, this method has become more acceptable for the determination of several long-lived radionuclides such as  $^{232}Th$  ( $1,39 \times 10^{10}$  years),  $^{238}U$  ( $4,47 \times 10^9$  years),  $^{235}U$  ( $1,75 \times 10^5$  years),  $^{230}Th$  ( $7,52 \times 10^4$  years) and  $^{234}U$  ( $2,48 \times 10^5$  years) owing mainly because it is faster.

Therefore, the aim of the present work was establish an analytical procedure, faster than the alpha spectrometry, designed for the control of  $^{230}Th$  contamination in phosphoric acid fertilizer and by-products for Santa Quitéria project, and comparing the results obtained by ICP-OES, ICP-MS and spectrophotometry with arsenazo III, as alternative methods, for elementary uranium and thorium determinations (practically corresponding  $^{238}U$  and  $^{232}Th$ ).

## 2. MATERIAL AND METHODS

### 2.1. Instrumentation

Determinations of uranium and thorium and  $^{230}\text{Th}$  isotope were performed using a Perkin-Elmer NexIon ICP-MS. A sequential Varian Liberty ICP-OES and a Varian 55 UV-VIS spectrophotometer were also used for uranium and thorium determinations for a comparison of results with ICP-MS, as well as for chemical characterization of the samples. Tables 1 and 2 indicate, respectively the operating conditions of the ICP-MS and ICP-OES. The spectrophotometric determinations of uranium and thorium with arsenazo III, adapted of Savvin [13], were performed as described in the "Procedimentos Normativos do Sistema de Gerenciamento da Qualidade do Laboratório de Poços de Caldas" [14].

**Table 1: Perkin-Elmer NexIon ICP-MS operation conditions**

RF Power	1480 W
Plasma gas flow rate	18 L min <sup>-1</sup>
Auxiliary gas flow rate	1.2 L min <sup>-1</sup>
Nebulizer gas flow rate	0.96 L min <sup>-1</sup>
Scan mode	Peak hopping transient
Lens scanning	Enable
Detector mode	Dual-pulse and analog
Dwell time	50 ms
Sweeps/Reading	30
Reading replicates	3 ( $^{230}\text{Th}$ ), 1 ( $^{238}\text{U}$ , $^{232}\text{Th}$ )
Number of replicates	3 ( $^{230}\text{Th}$ ), 5 ( $^{238}\text{U}$ , $^{232}\text{Th}$ )
Resolutions	0.7 amu at 10 peak max.
Signal processing	Spectral peaks integrated

**Table 2: Sequential Varian Liberty ICP-OES operation conditions**

RF Power	1300 W
RF generator	40 MHz
Plasma position radial	Vertical: 15; horizontal: 0
Nebulizer	Glass, cross-flow
Plasma gas flow	15 L min <sup>-1</sup>
Auxiliary gas flow	0.2 L min <sup>-1</sup>
Nebulizer gas flow	0.8
Sample intake	1.2 mL <sup>-1</sup>
Integration time	10 s
Number of replicates	3

### 2.2. Certified Solutions and Chemicals

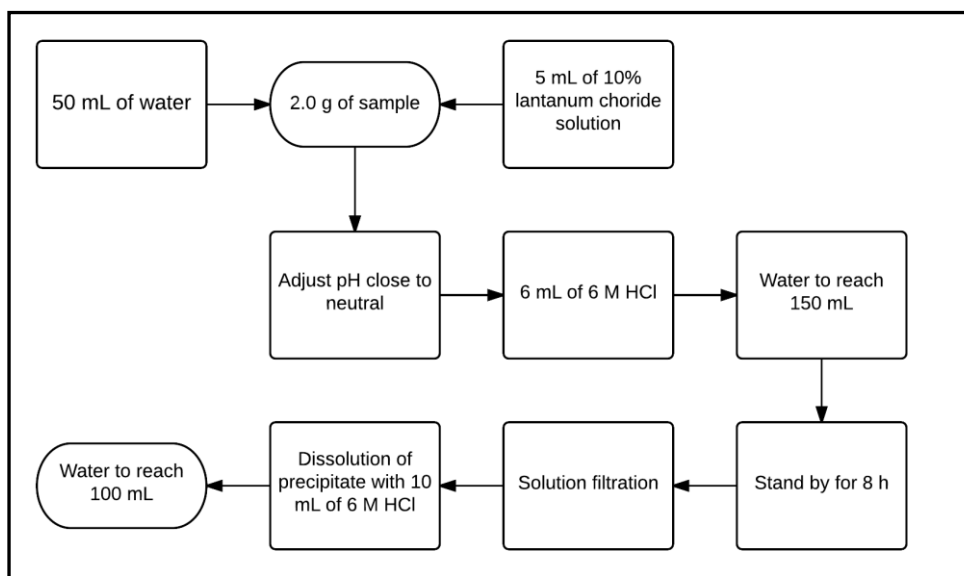
Uranium, thorium and others metallic ion certified solutions of  $1000 \mu\text{g L}^{-1}$  were supplied by AccuStandard, New Haven-CT, USA. The  $^{230}\text{Th}$  certified solution of 1746 Becquerel (Bq)  $\text{L}^{-1}$  was supplied by the Dosimetry and Radioprotection Institute, IRD, CNEN, Rio de Janeiro-RJ, Brazil. All other chemicals were of reagent grade and the purified water was suitable for ICP-MS analysis.

### 2.3. Samples Preparation

The samples used in this study were obtained from a pilot test process run carried out with Santa Quitéria phosphate rock. Identification and description of the analyzed samples are indicated on Table 3.

**Table 3: Coding and description of the analyzed samples**

Sample coding	Description
PAUTh	Phosphoric acid with uranium and thorium
R1PATH	Phosphoric acid after uranium removal
R2PATH	Aqueous phase after extraction of phosphoric acid
FGPA	Food grade phosphoric acid
R3FA	Phosphoric acid after thorium removal
STh	Sludge from thorium extract treatment



**Figure 1: Flowing process used for  $^{230}\text{Th}$  separation in phosphoric acid with uranium sample**

In all samples,  $^{230}\text{Th}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  were directly determined after dilution - except  $^{230}\text{Th}$  in phosphoric acid with uranium sample (PAUTh) which to overcome equipment contamination effect, was determined after its separation by oxalate precipitation using lanthanum as a carrier, based on routine method applied to rare earth elements gravimetric analysis [14]. The flowing process used for  $^{230}\text{Th}$  separation of PAUTh sample is shown in Figure 1. In the

direct analysis sample solutions  $10 \text{ g L}^{-1}$  were prepared for determination by ICP-OES and  $1.0$  or  $2.0 \text{ g L}^{-1}$  for ICP-MS and arsenazo III spectrophotometric methods. The sample solution were, when necessary, conveniently diluted according to the calibration concentration range.

### 3. RESULTS AND DISCUSSION

Table 4 indicates the results of  $^{230}\text{Th}$  determination in phosphoric acid fertilizer and in other process samples using the proposed method by ICP-MS and alpha spectrometry. Both ICP-MS procedures, for direct determination and separation and thorium separation by precipitation with oxalate proposed in this work, presented values in agreement in relation to those obtained by alpha spectrometry.

**Table 4:  $^{230}\text{Th}$  values obtained in phosphoric acid fertilizer and process products by ICP-MS (proposed method), as well as those obtained by alpha spectrometry. Values in  $\text{Bq g}^{-1}$**

Sample	ICP-MS	Alpha spectrometry
PAUTh	$18.1 \pm 1.8$	$17.1 \pm 2.6$
R1PTh	$16.3 \pm 0.8$	$16.8 \pm 3.0$
R2PTh	$16.1 \pm 0.9$	$16.9 \pm 2.5$
FGPA	$1.6 \pm 0.3$	$1.4 \pm 0.3$
R3FA	$< 1$	$0.08 \pm 0.02$
STh	$411 \pm 12$	$402 \pm 60$

**Tabela 5: Chemical characterization of samples. Unless when indicated, values are expressed in  $\text{mg kg}^{-1}$**

Component	PAUTh	R1PTh	R2PTh	FGPA	R3FA	STh
$\text{P}_2\text{O}_5$	27.7%	27.1%	12.2%	18.0%	12.4%	15.1%
$\text{SO}_4$	0.770%	0.761%	0.665%	0.351%	0.531%	0.149%
Fe	1.01%	1.01%	0.892%	0.113%	47	31.2%
Al	0.625%	0.626%	0.191%	397	0.115%	1.16%
Ca	0.107%	0.107%	0.136%	74	0.145%	1.02%
Mn	697	649	772	42	825	310
Mg	838	872	745	87	3,9	2.44%
Zn	41	37	43	2.7	26	343
V	52	50	55	4.4	30	405
Ti	28	31	9.2	3.7	$< 0,5$	951
Cr	27	25	25	3.2	28	12
Cd	0.21	0.012	0.053	$< 0.01$	0,088	$< 0,01$
Cu	5.2	4.4	6.1	0.32	6.4	3.0
Ni	13.4	13.9	15.6	0.87	16.2	6.1
Pb	1.1	0.75	0.26	$< 0.1$	0.11	$< 0.1$

The analytical lines preferably selected for the determination of uranium and thorium by ICP-OES are 409.014 and 401.913 nm, respectively, once they suffer less interference of the most common macro (Fe, Al, Ca, Si, etc.) and minor components like rare earth elements and other heavy metals. However, from the methods employed in this work, ICP-OES is the most susceptible to interferences for the determination of elementary uranium and thorium. In this way, a chemical characterization of samples was performed, as indicated on Table 5, as to learn the concentration levels of components, in order to match the uranium and thorium calibration solutions with the addition of the major elements at levels of concentrations of the samples. The chemical characterization was performed by ICP-OES, except for SO<sub>4</sub> which was determined by barium chloride turbidimetry.

Table 6 presents the results of elementary thorium and uranium analyses performed by ICP-MS, ICP-OES and spectrophotometry with arsenazo III. The obtained values for thorium in the three methods presented satisfactory agreement among them. Concerning uranium, the results presented satisfactory agreement among the samples of highest concentration, while the most discrepant values were detected in the R2PATH sample in which the detected value of ICP-MS was 40% lower than the others. However, it should be stressed that the ICP-MS method, due to its greater sensitivity, is best suited for samples with low content.

**Tabela 6. Elementary Uranium and thorium analyses. Values are expressed in mg kg<sup>-1</sup>**

Sample	ICP-MS		ICP-OES		Arsenazo III Sp.	
	U	Th	U	Th	U	Th
PAUTh	1308 ± 53	127 ± 5	1329 ± 66	124 ± 6	1320 ± 159	122 ± 16
R1PATH	4.0 ± 0,4	114 ± 4	< 7	107 ± 5	< 10	121 ± 15
R2PATH	4.3 ± 0,2	123 ± 5	10 ± 2	125 ± 6	12 ± 3	127 ± 19
FGPA	4.4 ± 0,2	11.4 ± 0,6	< 7	11 ± 2	< 10	<10
R3FA	1.5 ± 0,2	2.6 ± 0,1	< 7	2.8 ± 0,3	< 10	< 10
STh	37.0 ± 1,5	2586 ± 103	< 70	2760 ± 126	40 ± 6	2528 ± 335

#### 4. CONCLUSIONS

The ICP-MS method established in this work proved to be suitable for <sup>230</sup>Th determination in phosphoric acid fertilizer and other process samples when compared to the values from alpha spectrometry, with advantage of being a faster technique which presents lower result uncertainty.

After comparing results of elementary uranium and thorium from ICP-MS to ICP-OES and spectrophotometry with arsenazo III, it may be concluded that the values observed were in good agreement except in the case of uranium in a sample whose ICP-MS value was 40% lower than the others.

Depending on instrumental availability of process control laboratory, the method by ICP-MS would be the most suitable for the determination of uranium and thorium in samples with lower content (< 10 mg kg<sup>-1</sup>), thus preventing its use in high concentration samples that may cause equipment contamination. More concentrated samples could be analyzed by ICP-OES

or spectrophotometry with arsenazo, however ICP-OES would be more advantageous because it is faster and with less uncertainty values.

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