

QUANTITATIVE ANALYSIS OF THORIUM IN THE PRESENCE OF RARE EARTH BY X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

The occurrence of Thorium in ores is normally associated to other elements such as Uranium and Cerium, as well as some Rare-Earths (RE). The separation of these elements by traditional analytic chemistry techniques is both time and reagent consuming, thus increasing the analysis cost. The hereby proposed method consists in the direct determination of Thorium in rare earths ores and compounds by X-ray fluorescence spectroscopy without any prior chemical separation from other matrix elements. This non-destructive technique is used to determine which elements are present in solid and liquid samples, as well as their concentrations. The studied matrix contains Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Gadolinium and Yttrium. This study evaluated the analytical lines of radiation emission for each rare earth contained in the matrix, comparing it to the Thorium main analytical line. The Thorium quantification was measured through the Th $L\alpha$ line, where there is no influence or interference from the rare earths analytical lines. The studied samples are certified standards and the obtained results have been compared to Ethylenediaminetetraacetic acid (EDTA) titration results, an already well-established and widely trusted method. We also measured the matrix effect thus using complex rare earths liquor. This liquor contains also elements commonly found in monazites sands: phosphates, aluminum, iron. Obtained results state the efficiency of X-ray Fluorescence to determine Thorium in the presence of rare earths without any prior chemical separation.

1. INTRODUCTION

Currently there are several analytical methods able to reproduce excellent results for the quantification of Th in complex matrices coming from ores.

Instrumental techniques of high precision are usually applied to the determination of low concentrations of Th.

However, in cases of pre-concentration of rare earths ores, the amount of Th that is usually associated with ores of REEs is also pre-concentrated with the other elements. At the end of the process, the REEs liquor becomes a complex matrix with high concentration of Th.

Classical methods such as titration with DTPA do not produce satisfactory results without prior separation of Ce IV and U [1].

Instrumental Methods and inductively coupled plasma atomic emission spectrometry (ICP-AES) apply to low concentrations of Th starting at 2 ppm; however, require complete separation and purification of U, seriously interfering in this analysis [2].

The implementation techniques of XRF analysis in REEs is widely used, for allowing the quantification of individual REE without prior separation between them [3].

The use of Synchrotron-induced EDXRF is also applied for the measurement of U and Th in oxides using Y as internal standard[4].

The method described in this paper presents a quantification of Th applied in complex matrix containing lightweight REEs as well as U. The samples are liquid, in the midst [0.050 mol L⁻¹] in HCl. Analysis instrument used was EDXRF.

2. EXPERIMENTAL

2.1. Reagents and Solutions

We used the following reagents and materials: Lanthanium oxide, Cerium oxide, Neodymium oxide, Samarium oxide, Gadolinium oxide, Yttrium oxide and Uranium oxide (Johnson Matthey Chemicals Limited), Praseodymium oxide (SPEX – Industries, INC.), Thorium nitrate, EDTA and methylene blue (Merck), hydrochloric acid (Isofar), 2.27 mg.cm⁻² filter paper disc with 0.9 mm Ø (J.PROLAB), film with 55 µm thickness (Mylar™).

2.2. Instrumentation

A Shimadzu, model EDX-800HS, dispersive energy X-Ray Fluorescence Spectrometer (EDX) with a silver anode X-Ray tube operated at 40 KV and 30 mA, a LiF analyzer crystal and a NaI-Tl scintillation detector were used in all determinations.

2.3. Sample preparation

All solutions were prepared from analytical-grade reagent. Tri-distilled water was used in all dilutions. Thorium and REEs solution were obtained by dissolving their salt or oxide with hydrochloric acid (Isofar). The solutions were standardized with EDTA and orange xylenol.

In order to analyze the matrix effect and the influence of REEs in the quantification of Th we prepared a solution containing the same concentration of all REEs under study (STANDARD MIX - SM). The concentration of each element in SM is shown in Table 1. A scan was performed in the standard mix containing rare earths and Th in order to identify potential analytical lines matching with other elements that could affect the measurement of Th in Lα1 (Figure 1).

Starting from a standard solution of Th measured by titration with EDTA and orange xylenol, a calibration curve - which concentration points are shown in Table 2 - was prepared. Still using SM, we performed a standard addition curve to quantify Th, in the presence of REEs.

The preparation used in all solutions to EDXRF analysis was as follows: 20 μ L of sample were carefully spotted in a filter paper disc support. Then the wet support was heated in a 200 watts lamp until it was dry (60 minutes). A protection Mylar™ was fixed into the support. The prepared material was analyzed by X-ray fluorescence.

3. RESULTS AND DISCUSSION

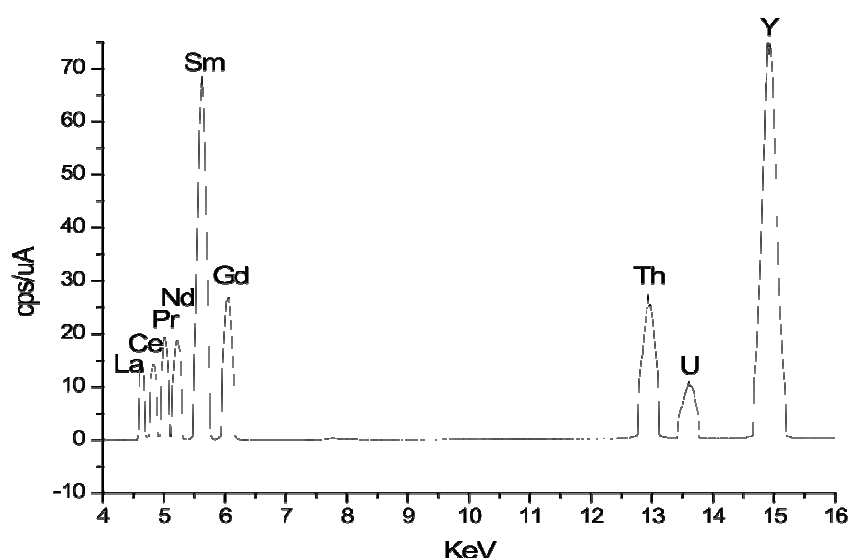


Figure 1: Scan of Standard Mix (REEs+Th)

Table 1: Chemical Composition of Standard Mix

REE	[REE] g.L ⁻¹	
Y	0.0075±0.01	(1.30%)
La	0.0074±0.01	(1.49%)
Ce	0.0077±0.01	(1.57%)
Pr	0.0078±0.01	(2.83%)
Nd	0.0075±0.01	(2.97%)
Sm	0.0076±0.01	(4.93%)
Gd	0.0075±0.01	(2.11%)
Th	8.5187± 0.01	(1.78%)

**Results are expressed as mean ± standard deviation (n = 5). Coefficient of variation is between parentheses.*

3.1 Evaluation of the effect matrix

The scan shown in figure 1 only considers La1 analytical lines of each element, and shows that the energy measured in La1 Th does not suffer interference from energy emitted by REEs in their respective La1. The signal measured for the minimum concentration of Th present in SM ($8.5187 \pm 0.0001 \text{ g L}^{-1}$) is widely distinguished from the recorded background.

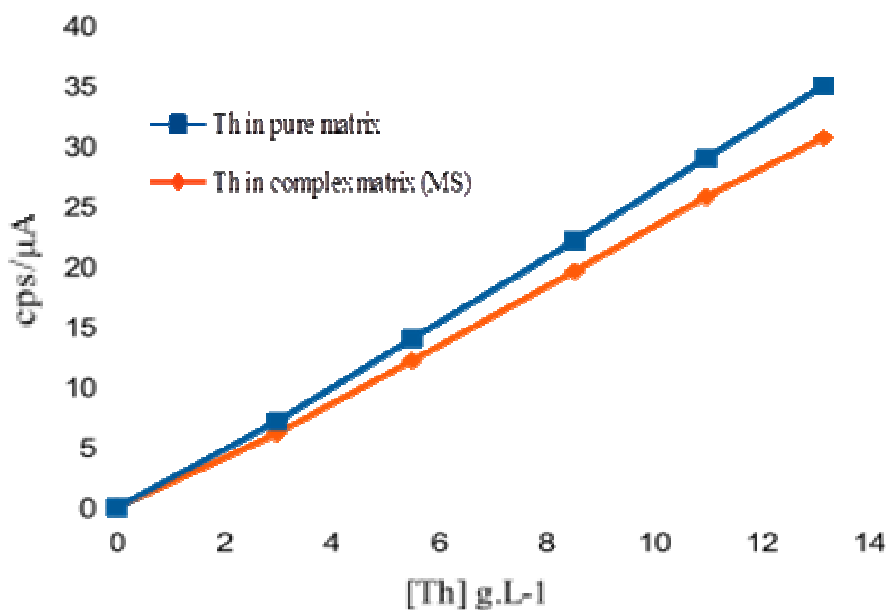


Figure 2 : Calibration Curve Th by EDXRF

Table 2: Values of [Th] at calibration curves

ID	[Th] g.L ⁻¹	CV	Cps/μA
Sample1	0.0000	(1.29%)	0.0000
Sample2	2.9714±0.01	(1.50%)	7.1254
Sample3	5.4897±0.01	(2.83%)	13.9878
Sample4	8.5187±0.01	(2.37%)	22.1265
Sample5	10.9679±0.01	(2.93%)	29.0000
Sample6	13.1531±0.01	(2.23%)	35.4871

*Results are expressed as mean \pm standard deviation ($n = 5$).

3.2 Quantification of Th by EDXRF simple matrix and complex matrix with REEs.

The calibration curve for Th pure matrix was obtained by adding 20 μL of standard solution with increasing concentrations of Th on 9 mm Φ paper discs. The calibration curve for Th in complex matrix was obtained using the same concentrations of Th, but on paper discs doped with 20 μL of standard mixed REEs (SM), both represent the range between 2.9714 and $13.1531 \pm 0.01 \pm 0.01 \text{ gL}^{-1}$ of Th.

The concentration of REEs at each point on the curve complex matrix is shown in Table 1 and the concentration of Th at every point of the two curves is shown in table 2.

Though figure 2 illustrates that the curve obtained from complex matrix showed lower signal, the matrix effect did not influence measurements for standards in La1 Th. The straight-line equation and correlation coefficient are shown in equations 1 and 2 described below:

$$\text{Cps}/\mu\text{A Th} = (2.6794 [\text{Th}]) - (0.4800) \quad \mathbf{R^2 = 0.9993} \quad (1)$$

Linear equation Th in pure matrix

$$\text{Cps}/\mu\text{A Th} = (2.7038 [\text{Th}]) - (0.5668) \quad \mathbf{R^2 = 0.9990} \quad (2)$$

Linear equation Th in complex matrix

4. CONCLUSIONS

The total time spent with the analysis of the Th by the proposed method was approximately 2 hours including the construction of the calibration curve. This time is much less compared to methods that require the Th solvent extraction or the use of ion exchange resins.

The results obtained are satisfactory for quantitation of Th at the concentrations shown and in the presence of U and REEs, considering the use the method of standard addition on the matrix under investigation. This method can be tested on solid samples as long as they are fixed on absorbent bases.

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