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OTHER RARE EARTH ELEMENTS IN THORIUM SOLUTION**

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# DIRECT SPECTROFLUORIMETRIC DETERMINATION OF CERIUM AND OTHER RARE EARTH ELEMENTS IN THORIUM SOLUTION

Raul J. Cazotti and Alcidio Abrão

## SUMMARY

The intense fluorescence emitted by Ce-III enables its determination directly in thorium solutions with high sensitivity and confidence. The determination of Ce-IV was studied in hydrochloric, perchloric and sulfuric acids, cerium exhibiting the same sensitivity in the three solutions. Although still high fluorescence is shown in sulfuric acid solutions, the determination of cerium in thorium sulfate solution is not recommended due to the low solubility of this salt.

The direct determination of cerium in thorium carbonate and thorium perchlorate is accomplished by excitation at 257 m $\mu$  and measurement of the intense emission fluorescence band at 350 m $\mu$ . The method allows the determination of cerium as low as 0.01 ppm Ce/Th. The linearity of the determination is obeyed from 0.001 to 100  $\mu$ g Ce/ml solution.

The quenching effect of thorium was studied. Solutions as high as 200 g Th/liter reduce to 20% the fluorescence of cerium, but even so it is possible to determine 0.004  $\mu$ g Ce/ml in solution of 200 g Th/liter (0.02 ppm Ce/Th).

Considering that the separation of cerium from thorium is not required and that only a few elements interfere, the method is fast and accurate.

The paper describes also the fluorimetric determination of other lanthanides in thorium chloride or thorium perchlorate. Terbium, europium and gadolinium exhibited intense fluorescence in dilute solutions of inorganic acids, and can be determined directly in thorium solutions starting from 50  $\mu$ g Tb/g Th, 80  $\mu$ g Eu/g Th and 200  $\mu$ g Gd/g Th.

The paper gives details for the direct determination of cerium, terbium, gadolinium and europium in dilute inorganic acid and in thorium solutions.

## INTRODUCTION

The increasing interest of thorium use in nuclear reactors for production of the fissionable uranium-233 nuclide, as is the case of high temperature gas cooled reactors, required the production of highly pure thorium. Usually the thorium concentrates are obtained from monazite and as a consequence the rare earth elements are the most serious accompanying elements. The analytical chemist has to face the situation of determining extremely low concentration of rare earths in pure thorium compounds, specially those of high cross section for thermal neutron. It is well known that the determination of traces of lanthanides in pure thorium is quite laborious and presents many difficulties, even when the analytical technique is the emission spectrographic one. Besides that, in the great majority of existing procedures a previous separation of lanthanides from thorium, again of difficult accomplishment, is required.

An analytical procedure for the determination of at least some of the rare earth elements directly in thorium solutions, with no chemical separation, and presenting high

sensitivity and specificity would be very much desired. Such a convenient procedure is performed by direct spectrofluorimetric determination as described in this paper.

In the solvent extraction purification of thorium using tributylphosphate (TBP) - Kerosene as extractant for thorium nitrate the next element extracted as impurity is cerium whose distribution ratio is the highest considering all the rare earth elements. In this way the determination of cerium in purified thorium will give, with reasonable approximation, the high limit for all rare earths co-extracted with thorium. The direct spectrofluorimetric determination of cerium in thorium solutions as proposed here allowed this control in a convenient, fast, simple and sensible manner.

Other rare earth elements that fluoresce with relative intensity in inorganic acid solution are gadolinium, terbium and europium, but only the last two can be determined directly in thorium solutions and will be described here.

## SPECTROFOTOMETRIC AND SPECTROFLUORIMETRIC TECHNIQUES APPLIED TO THE DETERMINATION OF RARE EARTH ELEMENTS

As a technique for the determination of traces in solutions the spectrofluorimetry has the fundamental advantage of a much higher sensitivity than the spectrophotometry; this high sensitivity counterbalances the greater number of interferences found in some spectrofluorimetric determinations.

Due to their great chemical resemblance the determination of one rare earth in the group of lanthanides by the conventional procedures is rather difficult. To overcome this difficulty techniques based on the physical characteristics of the lanthanides have been used as is the well known absorption spectrophotometry which uses the characteristic electron spectra of some rare earths in aqueous solutions<sup>11</sup>. Unfortunately this technique is not highly sensible. Among the rare earths cerium is quite unique in presenting an absorption band very intense in the ultraviolet region with a maximum in  $320 \text{ m}\mu^{2,3}$  which allows its determination with reasonable good sensitivity.

As an analytical technique for traces determination the spectrofluorimetry has been used more frequently in the last years. The fluorescence spectra of some rare earths in aqueous solutions such as for cerium<sup>4,7</sup>, terbium<sup>8,10</sup>, samarium<sup>8,10,12</sup>, europium, gadolinium, praseodymium and dysprosium<sup>11,14</sup> were published quite recently. The interest for the spectrofluorimetric technique increased not only in the search of methods for determination of vanishing small amount of lanthanides but also due to the improved new excitation sources covering greater region of the spectrum, mainly in the ultraviolet region (lower than  $300 \text{ m}\mu$ ), the best one for the rare earth elements determination. With the commercialization of new spectrofluorimeters of higher selectivity and sensitivity for excitation and fluorescence wave length, the fluorimetric technique is reaching a unique position among the instrumental analysis, specially for the rare earths determination. These elements are together with thorium and uranium, the only few ones that can fluoresce with relative high intensity in inorganic solutions without use of chelating or complexing ligands.

While the spectrophotometric methods are quite wide spread out, mainly for lanthanides whose electronic spectra absorb in the visible, but frequently used only for concentrations

higher than 20-50  $\mu\text{g/ml}$ , only a few methods based on spectrofluorimetric techniques have been published. Of these a fewer ones dealt with the fluorescence of rare earths in inorganic acid solutions. Alberti and Massucci<sup>8,10</sup> observed that certain ions like tungstate and oxalate increase the fluorescence of some lanthanides. It was observed that some lanthanides such as terbium presented reasonable high fluorescence in hydrochloric acid solutions<sup>12</sup> and the authors have observed the fluorescence of gadolinium and europium in HCl solution. But the great majority of spectrofluorimetric determination methods for rare earths use the aid of organic ligands for the formation of fluorescent chelates.

Of the rare earths group, cerium is one that presents the strongest fluorescence in aqueous inorganic solutions and this property was used by the authors for its determinations in thorium solution and in rare earths concentrates as well. Only about ten years ago was the Ce-III fluorescence<sup>16</sup> observed in inorganic acid solutions such as HCl,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$ . In one paper<sup>17</sup> where the spectrofluorimetric determination of thallium in HCl solutions was studied, the fluorescence of Ce-III was observed and mentioned as one of the few interferences.

Armstrong et al<sup>18</sup> observed the intense fluorescence of Ce-III in  $\text{H}_2\text{SO}_4$ , with an excitation maximum at 260  $\text{m}\mu$  (secondary peak at 295  $\text{m}\mu$ ) and a fluorescence maximum at 350  $\text{m}\mu$ . It was observed also that the fluorescence of cerium was not affected by the concentration of sulfuric acid in the 0.02 - 1.0M range, allowing its determination in pure solutions at level as low as 0.002  $\text{mg/l}$ . The same authors studied the interference of other rare earths and concluded that only Ce-III fluoresces in pure HCl and  $\text{H}_2\text{SO}_4$  solutions. However studying systematically the fluorescence of each one rare earth elements in the present work we could note that Tb-III, Eu-III and Gd-III exhibit quite intense fluorescence in sulfuric, perchloric and hydrochloric acid solutions.

Kirkbright et al<sup>14</sup> used the property of only Ce-III being fluorescent in sulfuric medium while Ce-IV does not fluoresce, for the indirect determination of some ions like As-III, Fe-III, Os-VIII, oxalate and iodide. The same authors also used the fluorescence of Ce-III in perchloric acid for its determination in yttrium oxide.

## FLUORESCENCE OF Ce-III IN INORGANIC ACIDS

We studied systematically the fluorescence of Ce-III in various inorganic solutions, including hydrochloric, perchloric and sulfuric acid and concluded that it fluoresces equally with high intensity in the last three solutions. In these acids Ce-III exhibits an excitation maximum at 257  $\text{m}\mu$  (with a secondary peak at 300  $\text{m}\mu$ ) and a fluorescence maximum at 350  $\text{m}\mu$  (with a less intense band at 280  $\text{m}\mu$ ). While the determination of cerium in pure solutions of HCl,  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  does not present any problem, for the determination of cerium in thorium solution only the first two acids should be considered. Although still high fluorescence is shown in sulfuric acid solutions, the determination of cerium in thorium sulfate solution is not recommended due to the low solubility of this salt.

## EXPERIMENTAL PART SPECTROFLUORIMETER

All intensity fluorescence measurements and excitation fluorescence spectra were recorded with a Perkin Elmer Fluorescence Spectrophotometer model MPF-2A with 15 watts

xenon lamp and a photomultiplier tube, with a Hitachi Recorder QPD-33. All measurements were performed using 10.00 mm quartz cell (101-QS).

## REAGENTS

All solutions were prepared using spectrographic standards and demineralized water bidistilled in quartz apparatus.

A 200 g Th/l solution was prepared by dissolution of a specpure  $\text{ThO}_2$  (Johnson Matthey-Chemicals Ltd., England, Specpure  $\text{ThO}_2$ , Catalogue JMC-490, Laboratory n<sup>o</sup> S-502B-D) with hot HCl catalized by HF. After complete solubilization the solution was evaporated three times until sirup and diluted to 0.5M HCl. This stock solution was analyzed for cerium and it was found to be less than 0.1 ppm Ce/Th.

Rare earth solutions were prepared by dissolution of Specpure oxides with HCl or  $\text{HClO}_4$  acid and diluted to a convenient concentration.

## CERIUM EXCITATION AND FLUORESCENCE SPECTRA

Figure 1 depicts the excitation and fluorecence spectra of a 2 mg/l Ce-III solution in 0.5M HCl. These spectra were recorded with excitation at 257 m $\mu$  (excitation maximum for Ce-III in this solution) and the maximum of fluorecence was recorded at 350 m $\mu$  (maximum fluorecence). The maximum of excitation was recorded with the measurement of fluorecence at 350 m $\mu$ .

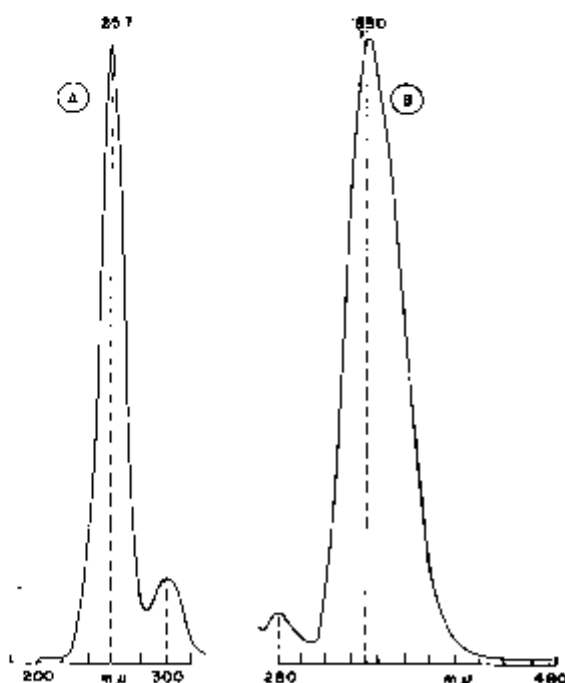


Fig. 1 - Excitation (A) and fluorecence (B) spectra of a pure cerium solution (2 mg/l) in hydrochloric medium.

Figure 2 depicts the emission fluorescence spectra of a 2 mg Ce/l solution in a 100 g Th/l solution, that is, a 20  $\mu$ g Ce/g Th in 0.5M HCl (Fig. 2A) and in 0.5M HClO<sub>4</sub> (Fig. 2B), respectively. Both spectra were recorded at the same experimental conditions with excitation at 257 m $\mu$ .

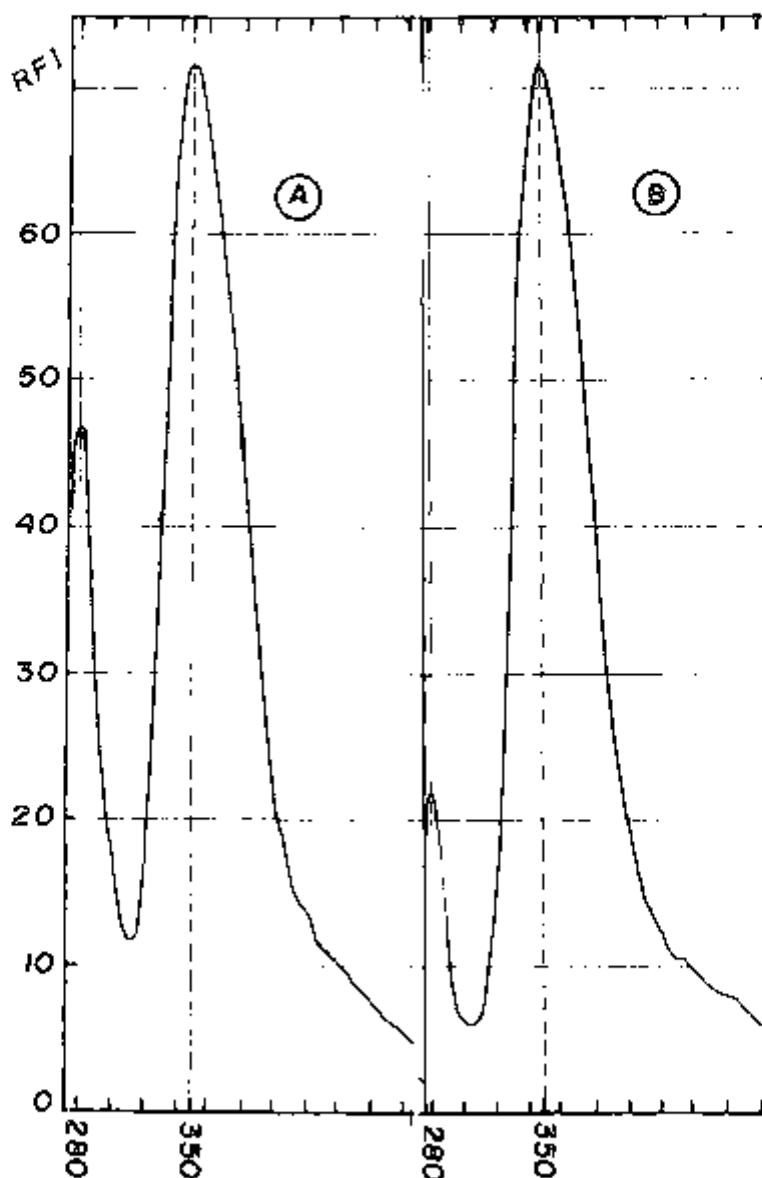


Fig. 2 - Emission spectrum of a solution with 2 mg Ce/l and 100 g Th/l in the hydrochloric (A) and perchloric (B) media.



In the purification processes thorium is commonly handled as thorium nitrate. Unfortunately in this medium it is not possible to observe the excitation and fluorescence spectra of Ce-III since the nitrate ion is a high absorber of ultraviolet radiation even at very low concentration and causes quenching of the cerium fluorescence.

### CERIUM CALIBRATION CURVES

Figure 3 depicts the calibration curves for cerium-III directly in thorium chloride and perchlorate, respectively, both being practically coincident. The fluorescence of cerium was recorded in the 0.0 to 0.065 mg/l range in a solution of constant thorium concentration (50 g  $\text{ThO}_2/\text{l}$ ), that is, from 0.0 to 1.3 ppm  $\text{Ce}_2\text{O}_3/\text{ThO}_2$ . For the practical determination of cerium in thorium solutions the  $\text{ThO}_2$  concentration can be maintained at fixed concentration ranging from 10 to 400 g  $\text{ThO}_2/\text{l}$ .

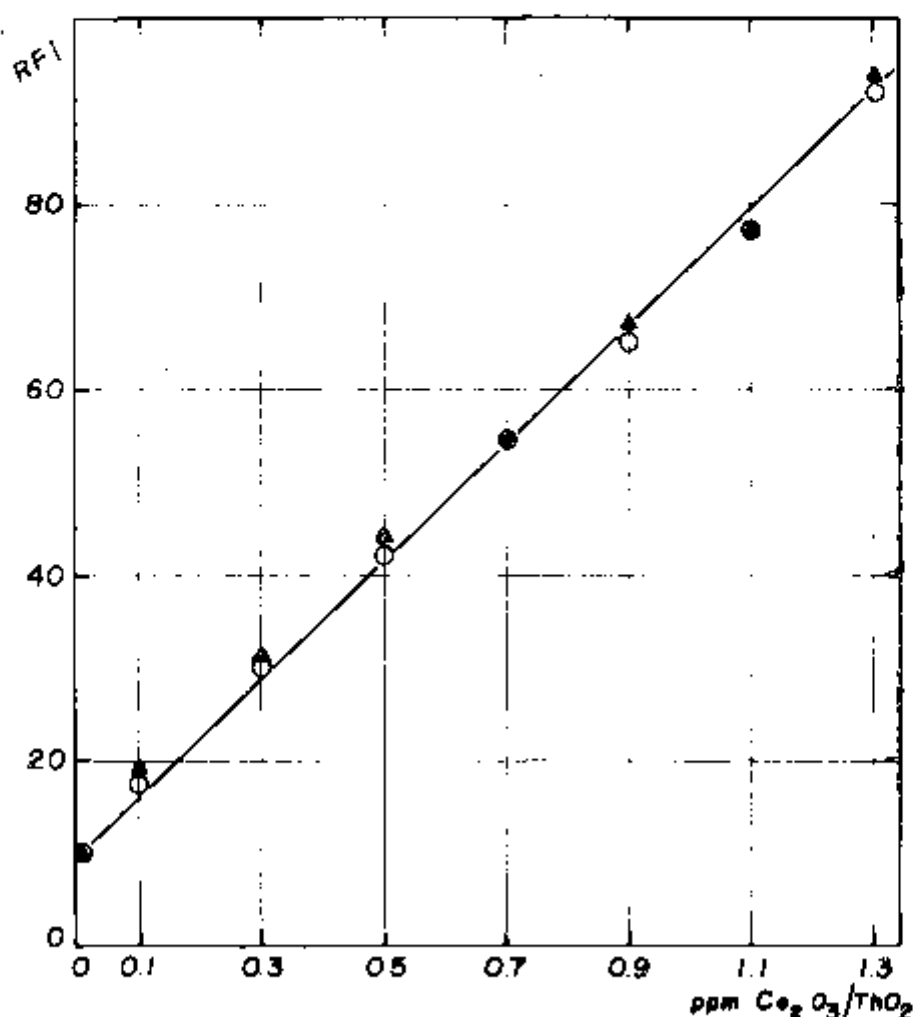


Fig. 3 - Calibration curve: ppm  $\text{Ce}_2\text{O}_3/\text{ThO}_2$  vs. Relative Fluorescence Intensity.

○ -  $\text{HClO}_4$

▲ -  $\text{HCl}$

## QUENCHING EFFECT OF THORIUM

The determination of very low amounts of cerium in thorium solutions requires a high content of thorium. For this reason the quenching effect of thorium in the cerium fluorescence was studied for thorium concentration ranging from 10 to 200 g Th/l. Figure 4 shows this effect.

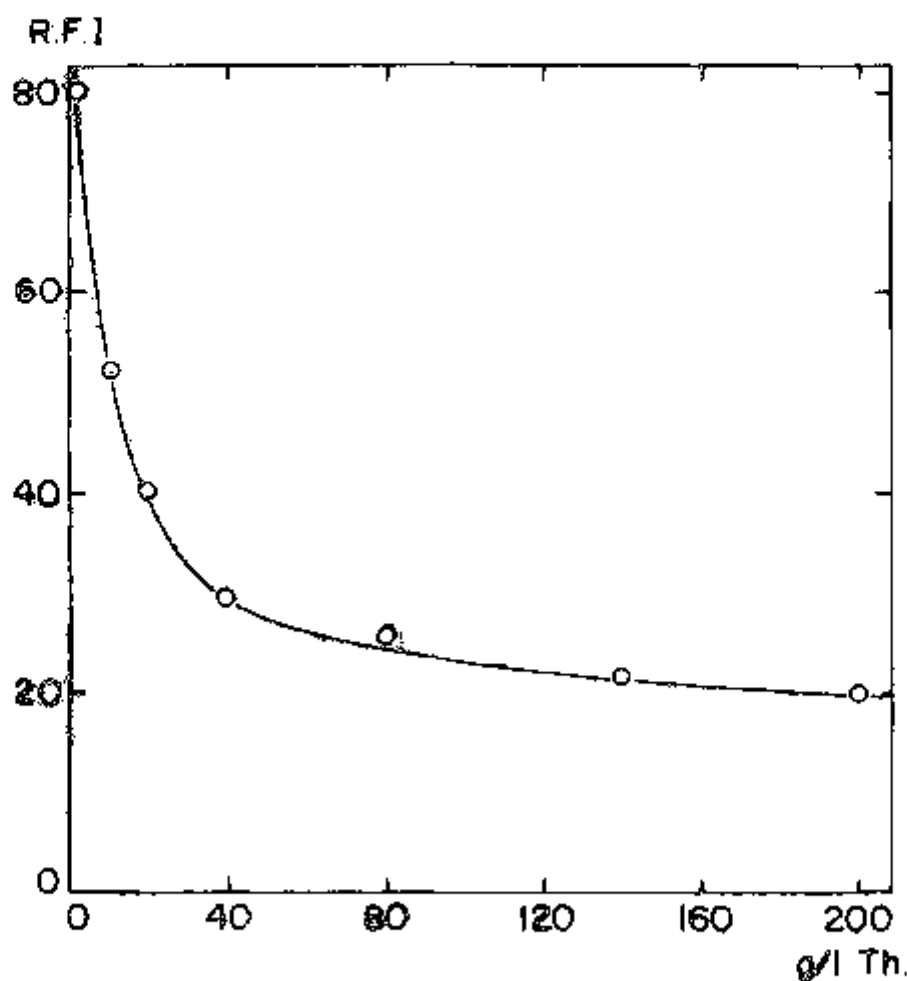


Fig. 4 - Effect of the Th concentration on the Ce emission fluorescence.

This curve was traced for constant cerium concentration of 0.1 mg Ce/l in 0.5M HCl and thorium concentration ranging from 0 to 200 g Th/l. As can be observed the quenching of cerium fluorescence by thorium is marked from 0 to 40 g Th/l, when the intensity of the fluorescence decays about 70% of its original value. From 40 to 200 g Th/l the quenching of cerium fluorescence is much less. This observation allows us to conclude that the sensitivity for the fluorimetric determination of cerium in thorium is higher for solutions of higher concentration of thorium.

## INTERFERENCES

Kirkbright et al.<sup>4/</sup> had shown that Cu-I, Pb-II and Sn-II ions exhibit some fluorescence in HCl solutions, but their fluorescence could be an interference only when these metals are present at concentration over 500 mg/l. The thorium solutions used in this paper were completely free from those metals. Tb-III presents relatively intense fluorescence in HCl solutions but its fluorescence peak is at 545 m $\mu$ , that is, considerably far from the Ce-III (350 m $\mu$ ), and does not constitute interference.

Cukor and Weberling<sup>5/</sup> studied the interference of various cations including the rare earths and Cu-II, Ni-II, Pb-II, Fe-III, and nitrate in the microdetermination of cerium in yttrium perchlorate and found that the most serious are Fe-III and NO<sub>3</sub><sup>-</sup>. These two ions when present in concentration 50 times that of cerium reduced drastically the fluorescence of cerium.

For the determination of cerium in HCl or HClO<sub>4</sub> media we found that the most serious interferences are Fe-III, NO<sub>3</sub><sup>-</sup> and UO<sub>2</sub><sup>++</sup> the two first absorbing strongly in the ultraviolet region (257 m $\mu$ ) and causing greater quenching. Nitrate can be eliminated by several evaporations with HCl or HClO<sub>4</sub> acid. Other ions that could interfere are sulfate, phosphate and fluoride that cause thorium precipitation and must be avoided. The interference of Fe-III is easily minimized by its reduction to Fe-II with hydroxylamine Hydrochloride, the ferrous ion not interfering. Uranyl ion interferes only at concentration higher than 20 mg/l, absorbing in the ultraviolet region.

Ce-IV that absorbs some radiation near to 257 m $\mu$  and absorbs also some radiation from the emitted fluorescence of Ce-III at 350 m $\mu$  is an interference in the determination of Ce-III but does not constitute any problem, being easily reduced with hydroxylamine.

Table I shows the interferences of the most probable ions encountered in the thorium solutions.

TABLE I

Interferences in the determination of cerium. 0.85 mg  $Ce_2O_3/l$  in 0.5M HCl.  
Excitation: 257  $m\mu$  and fluorescence: 350  $m\mu$ .

| ion      | mg/l | Relative Fluorescence Intensity (%) | variation (%) |
|----------|------|-------------------------------------|---------------|
| Ce - III | 0.85 | 100                                 | -             |
| La - III | 500  | 100                                 | 0             |
| Pr - III | 500  | 100                                 | 0             |
| Nd - III | 500  | 100                                 | 0             |
| Sm - III | 500  | 100                                 | 0             |
| Eu - III | 500  | 100                                 | 0             |
| Gd - III | 500  | 101                                 | +1            |
| Dy - III | 500  | 98                                  | -2            |
| Tb - III | 500  | 98                                  | -2            |
| Er - III | 500  | 99                                  | -1            |
| Tm - III | 500  | 102                                 | +2            |
| Yb - III | 500  | 102                                 | +2            |
| Ho - III | 500  | 100                                 | 0             |
| Lu - III | 500  | 102                                 | +2            |
| Fe - III | 20   | 90                                  | -10           |
| Fe - III | 2    | 98                                  | -2            |
| U - IV   | 20   | 95                                  | -5            |

#### APPLICATION TO THE DETERMINATION OF CERIUM IN SPECURE THORIUM OXIDE STANDARDS

Fig. 5A depicts the spectrum of a 200 g Th/l in 0.5M HCl and containing less than 0.1  $\mu g$  Ce/g Th and used as standard for all experiments in this paper.

Fig. 5B depicts the spectrum of another 200 g  $ThO_2/l$  solution in 0.5M HCl and prepared by the dissolution of a second spectrographic thorium oxide standard (Johnson

Mathey Chemicals Ltd., England, Specpure, Catalogue JMC-490, Laboratory n<sup>o</sup> S-51548-D) whose cerium concentration was determined by the procedure here described and found as  $1.1 \mu\text{g Ce/g Th}$ . Those specpure thorium oxide standards do not include cerium in their analysis certificate. The determination of cerium in various of those specpure thorium oxide standards indicated different cerium content, ranging from less than  $0.1$  to  $2 \mu\text{g Ce/g Th}$ .

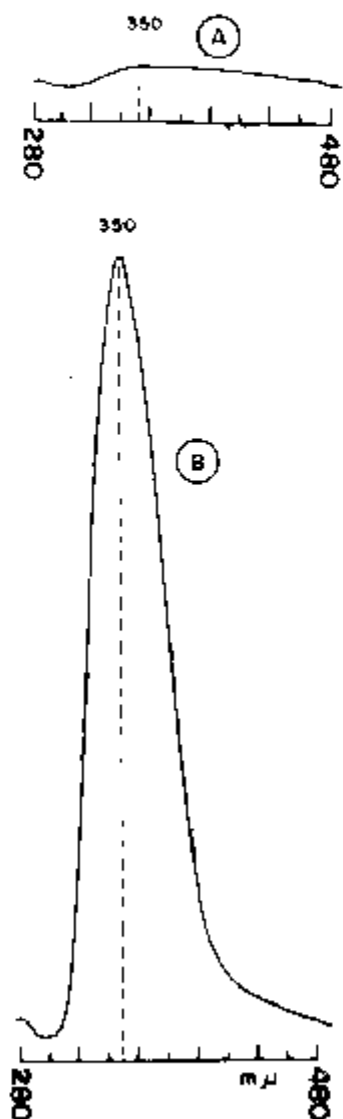


Fig. 5 - Emission spectra of Th solutions  
(spectrographic standards)  
(A and B)

## FLUORIMETRIC DETERMINATION OF OTHER LANTHANIDES IN THORIUM

We measured systematically the fluorescence spectra of all rare earths elements in HCl, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions. Only gadolinium, terbium and europium should be considered here as feasible for determination in thorium solutions.

Of all other rare earths elements but cerium, only terbium and europium have sensitivity high enough to be determined directly at low concentration in thorium solution. Terbium presents a high fluorescence band at 545 m $\mu$ <sup>(1,2)</sup> in dilute inorganic acids as can be seen in Figure 6.

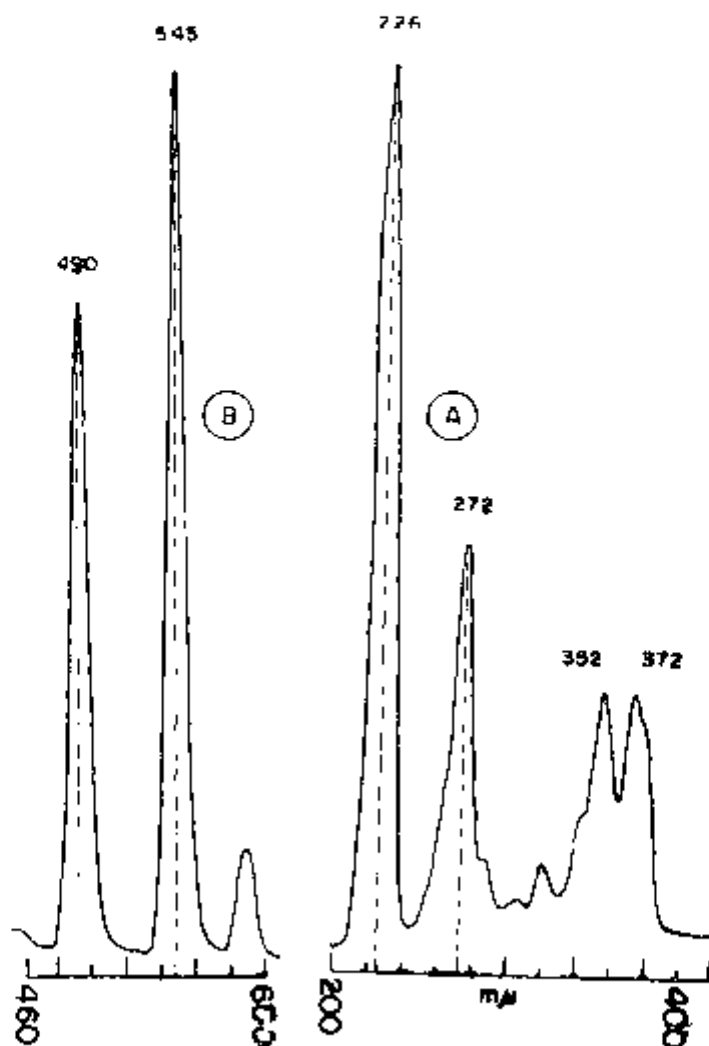


Fig. 6 - Tb: Excitation (A) and Emission (B) spectra in hydrochloric medium.

In the presence of thorium its emission fluorescence sensitivity is reduced since its most intense excitation peak is at 226 m $\mu$ , where thorium absorbs strongly. Figures 7A, 7B, 7C depicts the spectra of a 200 mg Tb/l in 0.5M HCl, a 2000  $\mu$ g Tb/g Th in 0.5M HCl and a pure 100 g Th/l in 0.5M HCl solutions, respectively.

The three spectra were recorded with excitation at 362 m $\mu$  (372 m $\mu$  can be used) and the fluorescence measured at 545 m $\mu$ ; the low detection limit was found as 50  $\mu$ g Tb/g in 200 g Th/l in 0.5M HCl solution.

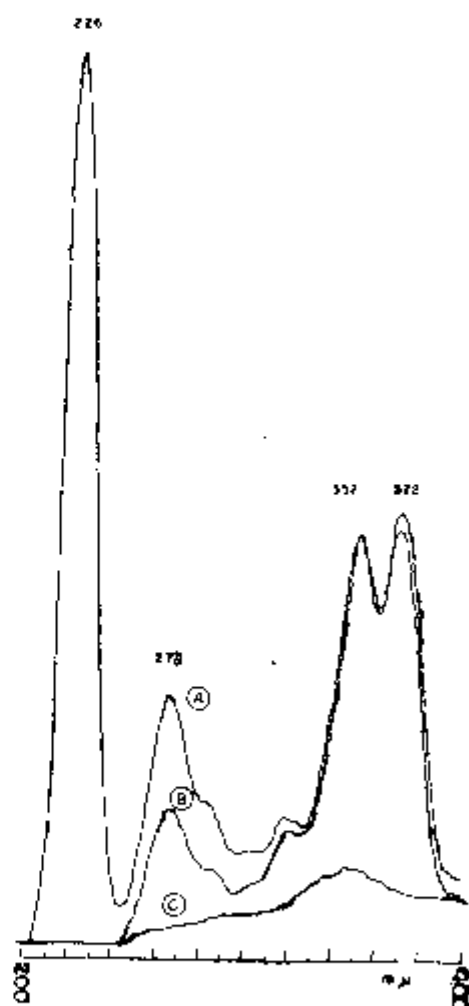


Fig 7 - Excitation spectra:

A - Tb (200 mg/l)

B - Tb (200 mg/l in 100 g Th/l)

C - Tb (100 g/l)

$\lambda_f = 545 \text{ m}\mu$

Europlum can be determined in pure inorganic acid solutions starting with 10 mg Eu/l. The excitation spectrum was recorded measuring the fluorescence at 595 m $\mu$  and the fluorescence spectrum was recorded with excitation at 394 m $\mu$  (Fig. 8). One band located at 395 m $\mu$  were observed in the excitation spectrum of Eu. A wide band at 453 m $\mu$  was observed in the fluorescence spectrum, but it does not belong to europium; a characteristic fluorescence band is exhibited by this element at 595 m $\mu$ .

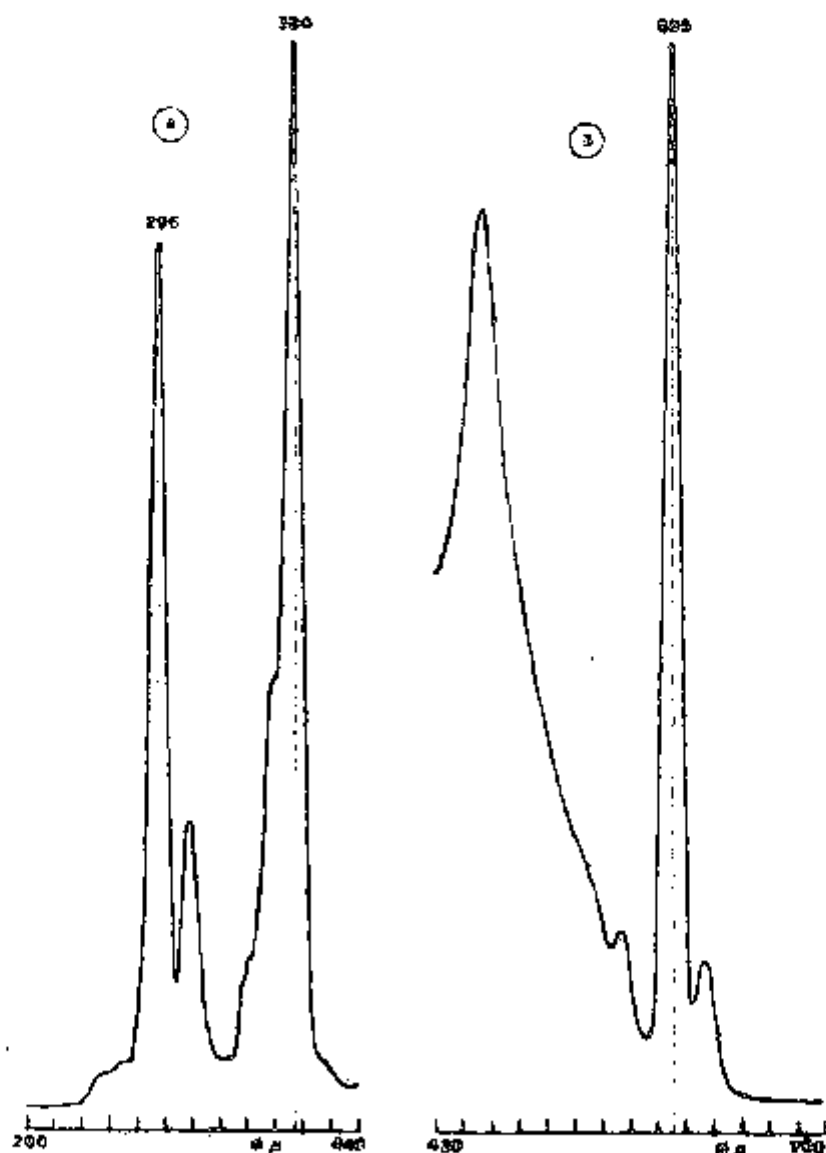


Fig. 8 - Excitation (A) and emission (B) spectra of a pure Eu solution (5 g/l) in hydrochloric medium.



For the direct determination of europium in thorium solution the lower limit was found as 100  $\mu$ g Eu/g Th in 0.5M HCl containing 200 g Th/l (Fig. 9).

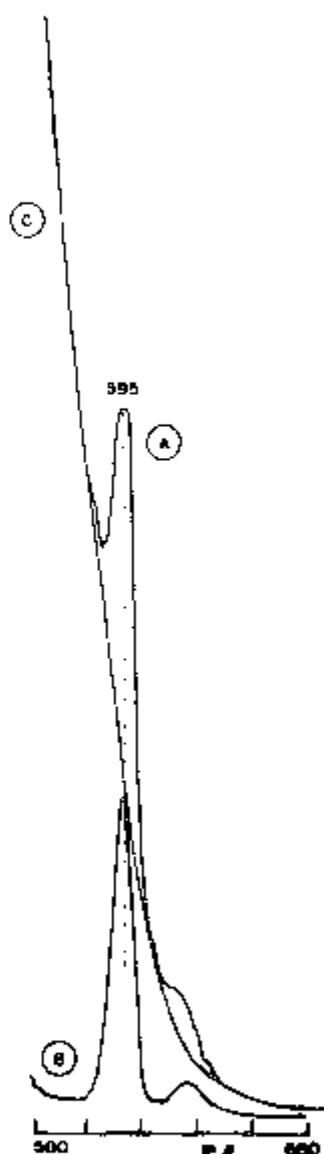


Fig. 9 - Fluorescence spectra of:  
A - 1 g/l Eu in 250 g Th/l  
B - 1 g Eu/l  
C - 250 g Th/l

In table II it can be seen the experimental conditions for direct spectrofluorimetric determination of RE in inorganic acids and thorium solutions.

TABLE II

Experimental Conditions for Direct Spectrofluorimetric Determination of RE  
in Inorganic Acids and Thorium Solutions

| El | Excit.<br>(m $\mu$ ) | Fluoresc.<br>(m $\mu$ ) | Detection Limit in: |  |
|----|----------------------|-------------------------|---------------------|--|
|    |                      |                         | HCl<br>( $\mu$ /ml) | ThCl <sub>4</sub><br>( $\mu$ g El/gTh) |
| Ce | 257                  | 350                     | 0,001               | 0,01                                   |
| Tb | 226,352 (372)        | 545                     | 0,5                 | 50                                     |
| Eu | 394                  | 595                     | 10                  | 80                                     |
| Gd | 275                  | 312                     | 10                  | 200                                    |
| Dy | 352                  | 480                     | 100                 | does not<br>fluoresce                  |

\* Excitation peak completely absorbed by Th.

## CONCLUSION

The direct spectrofluorimetric determination of Ce, Eu and Tb in highly pure thorium chloride or perchloride solutions was easily accomplished. Specially the intense fluorescence emitted by Ce-III enables its determination directly in thorium solutions with high and equal sensitivity in HCl and HClO<sub>4</sub> media. The method allows the determination of 0.01  $\mu$ g Ce/g Th. Although the quenching effect of thorium itself is quite considerable in the 1-40 g Th/l range, the determination of cerium is still possible at level as low as 0.002  $\mu$ g. Ce/ml in 200 g Th/l (0.01 ppm Ce/Th).

The fluorescence of lanthanide series in HCl, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> was systematically measured in the authors. Very intense fluorescence was exhibited by cerium. Its fluorescence is not affected by acid concentration in the 0.02-1 OM range, which is of great importance for the analyst.

The ease determination of cerium directly in thorium allows a reasonable approach for the indirect knowledge of total rare earths in thorium solutions proceeding from solvent extraction purification. This approach is given by the fact that Ce is the most extractable lanthanide in the TBP-HNO<sub>3</sub> extraction system. This is of paramount importance in the control of great number of samples in an industrial TBP-diluent thorium purification.

Tb, Eu and Gd fluoresce with relative intensity in inorganic acid media and can be

determined directly in thorium solution. The lower detection limits are 50  $\mu\text{g}$  Tb/g Th, 100  $\mu\text{g}$  Eu/g Th and 200  $\mu\text{g}$  Gd/g Th, in a 200 g/l Th solution in 0.5M HCl.

Considering that no chelating agents are necessary or the separation of Ce, Tb, Eu and Gd from thorium is not required, and that only a very few ions interfere, the method is fast, simple and accurate.

The most probable interferences found in thorium solutions handled in the purification system are Fe-III, Ce-IV,  $\text{NO}_3^-$  and  $\text{UO}_2^{++}$ , the three first being easily eliminated. Usually the thorium purified by TBP-diluent solvent extraction process has less than 20  $\mu\text{g}$  U/g Th and in this case the interference of uranyl ion is of less importance. (See Table I).

Ce, Tb, Eu and Gd can be determined in other rare earths concentrates as well. Experiments outlined for this demonstration is on progress.

## RESUMO

A intensa fluorescência emitida pelo elemento cério, em seu estado de oxidação III, permite sua determinação diretamente em soluções de tório, com alta sensibilidade e segurança. A determinação de Ce-III foi estudada em ácidos perclórico, clorídrico e sulfúrico, apresentando a mesma sensibilidade nas três soluções.

Mesmo apresentando intensa fluorescência em meio ácido sulfúrico, a determinação do cério em soluções de sulfato de tório não é recomendada devido à sua baixa solubilidade.

A determinação fluorimétrica de cério diretamente em soluções de cloreto ou perclorato de tório é realizada mediante excitação a 257 m $\mu$  e a medida de emissão fluorescente a 350 m $\mu$ , região de máxima fluorescência do cério nestas soluções. Por este método são possíveis determinações de cério em soluções de tório em concentrações tão baixas como 0,01  $\mu\text{g}$  Ce/g Th. A linearidade da determinação é obedecida de 0,001 a 100  $\mu\text{g}$  Ce/ml.

Foi estudado o efeito de supressão da fluorescência causada pelo tório. Concentrações tão altas como 200 g/l de tório reduzem a 20% a fluorescência do cério, sendo ainda possível, a determinação de até 0,004  $\mu\text{g}$  Ce/ml nessas soluções (0,02 ppm Ce/Th).

Considerando-se que não é necessária a separação de cério do tório, e que são poucas as interferências, o método é rápido e preciso.

O trabalho descreve também a determinação fluorimétrica de outras terras raras em soluções de tório. Térbio, európio e gadolínio apresentam fluorescência relativamente intensa em soluções diluídas de ácidos inorgânicos e podem ser determinados diretamente em soluções de tório, apresentando limites inferiores de detecção de 50  $\mu\text{g}$  Tb/g Th, 80  $\mu\text{g}$  Eu/g Th e 200  $\mu\text{g}$  Gd/g Th.

O trabalho fornece detalhes para a determinação fluorimétrica direta de cério, térbio, gadolínio e európio em ácidos inorgânicos diluídos e soluções de tório.

## RÉSUMÉ

La fluorescence intense émise par le Ce-III permet son dosage direct dans des solutions de sels de Thorium avec une grande sensibilité et de fiabilité. On a étudié le dosage du Ce-III dans des solutions dans les acides chlorhydrique, perchlorique et sulfurique, la sensibilité étant la même dans les deux premiers cas.

Dans le cas de la solution sulfurique, bien que la fluorescence soit forte, la méthode n'est pas recommandée en raison de la faible solubilité de ce sel.

Le dosage direct dans les chlorure et perchlorate de thorium est effectué par excitation à 257 m $\mu$  et mesure de la bande de fluorescence intense émise à 350 m $\mu$ . La méthode permet le dosage des teneurs de l'ordre de 0,01 ppm Ce/Th. Pour les teneurs allant de 0,001 à 100  $\mu\text{g}$  Ce/ml les résultats se présentent en

fonction linéaire

On a étudié l'effet absorbant du Thorium. Dans des solutions de l'ordre de 200 gr Th/litre la fluorescence du Ce est diminuée de 20%, mais il est encore possible de doser une teneur de 0.004 µg Ce/ml dans une telle solution soit 0.02 ppm Ce/Th.

Etant donné la séparation Ce/Th n'est pas nécessaire et qu'il n'y a que très peu d'éléments gênants, la méthode peut être considérée comme rapide et précise.

La communication décrit également l'analyse d'autres lanthanides dans des solutions de chlorure ou perchlorate de Thorium. Le Terbium et le Gadolinium présentent une fluorescence accusée en solution acide inorganique diluée et peuvent être dosés directement en présence du Thorium pour des teneurs à partir de 50 à 100 ppm Tb/Th dans HCl 0.5M. L'Europium donne également des fluorescences en milieu acide inorganique dilué et peut être dosé aussi bien en présence du Thorium.

La communication donne des détails sur le dosage mentionné ci-dessus.

## BIBLIOGRAPHY

1. T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 443 (1950).
2. A. I. Medalja and B. J. Byrne, *Anal. Chem.*, **23**, 453 (1951).
3. H. L. Greenhaus, A. M. Feibush and L. Gordon, *Anal. Chem.*, **29**, 1531 (1957).
4. G. F. Kirkbright, T. S. West and C. Woodward, *Anal. Chim. Acta*, **36**, 298 (1966).
5. P. Cukor and R. P. Weberling, *Anal. Chim. Acta*, **41**, 404 (1968).
6. W. A. Armstrong, D. W. Grant and W. G. Humphreys, *Anal. Chem.*, **35**, 1300 (1963).
7. G. F. Kirkbright, T. S. West and C. Woodward, *Talanta*, **12**, 517 (1965).
8. G. Alberti e M. A. Massucci, *Anal. Chem.*, **38**, 214 (1966).
9. Idem, *Anal. Chim. Acta*, **35**, 303 (1966).
10. Idem, *Gazz. Chim. Ital.*, **95**, 997 to 1021 (1965).
11. R. Belcher, R. Perry and W. I. Stephen, *The Analyst*, **94**, 26 (1969).
12. V. A. Fassel and R. H. Heidef, *Anal. Chem.*, **26**, 1134 (1964).
13. P. K. Gallagher, *J. Chem. Phys.*, **41**, 3061 (1964).
14. T. Taketatsu, M. A. Carey and C. V. Banks, *Talanta*, **13**, 1081 (1966).