

## Recent Advances and Actual Status of Actinides and Lanthanides Research at the IPEN–CNEN/São Paulo, Brazil\*

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### Abstract

This paper focuses on the experience acquired with the operation of a pulsed columns solvent extraction unit for the refining of yellowcake produced from the industrial treatment of monazite sand, and the further experimental production of ammonium diuranate, uranium oxides, uranyl tricarbonate and tetra- and hexafluorides of uranium at the pilot plant scale. Special studies have been devoted to the decontamination of the rare earth elements, thorium and zirconium.

The refining of thorium in a solvent extraction composite column and the experimental production of crystallized nuclear grade thorium nitrate at the pilot plant scale is also discussed. Thorium hydroxide sludges and crystallized thorium sulphate are used as raw materials, both produced from an alkaline breaking up monazite process.

Developmental efforts have also been directed towards the rare earth fractionation using as a first step previous chemical fractionation of the rare earth chlorides and the ion-exchange individual fractionation as the final process step to obtain extremely pure oxides.

Finally, the establishment of analytical procedures as an important support to the technical work is emphasized. An extended version of this work will be published elsewhere.

### Introduction

This paper reviews some of the main work on the conversion of yellowcake to nuclear grade products. The Institute of Nuclear Energy Research (IPEN, São Paulo) one of the CNEN institutes, is moving ahead on its plan to develop the fuel cycle. Starting

with yellowcake the whole process passes through pure ammonium diuranate (ADU), its calcination to uranium trioxide, followed by its reduction to  $UO_2$  with hydrogen generated by *in situ* cracking of ammonia gas. The next compound obtained is uranium tetrafluoride which is transformed into the hexafluoride in a flame reactor. Two other alternative technologies are under development: a denitration unit for experimental production of uranium trioxide; and an aqueous procedure to obtain uranium tetrafluoride.

The above-mentioned activities have been carried out at the pilot plant scale. Special care is devoted to the decontamination of the rare earth elements and thorium from the yellowcake produced by the industrialization of monazite sand, and the decontamination of zirconium from the uranium concentrate produced by the industrial processing of an uraniumiferous ore containing zirconium.

A pilot plant installed for the purification of thorium is in operation for the experimental production of high grade crystallized thorium nitrate, part of which is supplied to the local manufacturers of lamp mantles.

The experimental production of extremely pure lanthanide oxides has as scope the development of a technology for the installation of a facility to obtain individual rare earths (RE) based on a combination of techniques, the final refining being carried out by ion exchange. The fractionation of the RE starts with some previous chemical procedures for the production of enriched fractions from the rare earth chlorides mixture ( $RECl_3$ ). The final step is the refining through strong cation exchanger columns to which special emphasis was paid to develop a simplified process which does not use any retention ion, as is common practice today.

The development of new analytical procedures and the adaptation of known ones to local conditions have been carried out in support of the technical work: *i.e.*, the separation of extremely small amounts of thorium and rare earths in pure uranium; uranium and rare earths in pure thorium; and the determination of low contents of lanthanides in pure rare earth oxides.

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### Industrialization of Monazite and Raw Materials

The first yellowcake used at IPEN to obtain nuclear grade uranium products several years ago was sodium diuranate (SDU) produced from the industrial processing of monazite sand [1]. The chemical treatment for breaking up monazite sand by an alkaline process has been in practice in Brazil (São Paulo) since 1948 on an industrial scale [2]. The production capacity is about 3000 metric tons of monazite per year for the production of thorium, rare earth chlorides (2000 tons) and phosphates as the main products. After decontaminated from radium and its descendents by coprecipitation with barium sulphate, the lanthanides are commercialized as a natural mixture in the form of rare earth chlorides ( $\text{RECl}_3$ ) or as some enriched fractions. Thorium is stock-piled mainly as a crude hydroxide (thorium sludge). Uranium is recovered as a by-product in the form of SDU.

The main impurities considered in this yellowcake are sodium phosphate, silica, iron and, of course, thorium and rare earth elements. Great care is taken in the decontamination of thorium and lanthanides.

Recently a second yellowcake has been used at IPEN's installation. It comes from the Poços de Caldas Industrial Complex at Poços de Caldas, Minas Gerais State. This industrial plant is owned and operated by Nuclebrás. The yellowcake is ammonium diuranate of high quality, virtually free of thorium and rare earth elements. The only difficulty we had to cope with was the presence of zirconium contamination. After its dissolution with nitric acid, the uranyl nitrate was treated for the removal of the great majority of zirconium, before filtration to get a clear uranyl nitrate solution.

#### *Dissolution of Yellowcake*

For the purification of uranium the initial step is the dissolution of the concentrate with nitric acid to obtain a clear uranyl nitrate. During the dissolution most of the silica is removed by dehydration of silicic acid. The dissolution is accomplished in a stainless steel reactor in a batchwise fashion. The yellowcake is poured directly and slowly into the nitric acid. When all the yellowcake has been introduced its digestion is made by maintaining an acidity of 2 M  $\text{HNO}_3$  at 90–100 °C for the complete flocculation of silica.

If zirconium is present, the uranyl nitrate is treated with a controlled amount of phosphoric acid. Both silica and zirconyl phosphate are separated together. The hot pulp is filtered or centrifuged and the residue thoroughly washed for the removal of soluble uranyl nitrate. The filtered uranyl nitrate solution has a concentration of 475 g U/l and, after cooling, is adjusted to 300 g U/l and 1 M  $\text{HNO}_3$  previous to the solvent extraction. Sodium or ammonium nitrate, not less than 1 M, used as salting

out agent, is formed during the dissolution. In the case of the SDU produced from the monazite sand, the troublesome presence of Th and RE is minimized by the controlled addition of sodium sulphate prior to the purification of uranium by solvent extraction.

### TBP Extraction Pilot Plant for Purification of Uranium and its Conversion

A pilot plant facility set up for the purification of uranyl nitrate is based on the conventional liquid–liquid extraction technique using three pulsed columns for the extraction, scrubbing and stripping, respectively. The facility and its equipment, operational flow-sheet, performance and experience gained have been published [3]. A more detailed version of this work will be published elsewhere with more recent data covering the precipitation of nuclear grade ammonium diuranate (ADU), the conversion of uranyl nitrate into uranyl peroxide, and their calcining to  $\text{UO}_3$  oxide and its reduction to  $\text{UO}_2$  with hydrogen generated *in situ* by the cracking of  $\text{NH}_3$  gas using the uranium oxide as catalyst. The production of uranium tetrafluoride by both dry and wet methods and its conversion to uranium hexafluoride in a flame reactor will also be described. Also a review of the different techniques for the characterization of the solid compounds including thermoanalytical procedures such as TG, DTG and DSC (differential scanning calorimetry) will be covered.

#### *Cross-contamination of Uranium, Thorium and Lanthanides*

As mentioned before, the first problem to be solved was the presence of thorium (*ca.* 3%  $\text{ThO}_2$ ) and rare earths in the yellowcake. The lanthanides amounted to 0.3% and the high cross-section RE (Sm + Eu + Gd + Dy) had a content of *ca.* 0.02%/U.

The most economical and simple procedure for the decontamination of both thorium and lanthanides was the addition of sodium sulphate to the uranyl nitrate prior to the TBP–kerosene extraction of uranium. The spectrographic analysis of uranium oxide produced using the above-mentioned technique showed less than 1 ppm of total lanthanides (Ln). The main problem was not the spectrographical determination but the preconcentration and separation of the Ln from the bulk of the uranium; this was very nicely performed using a specially developed technique based on the retention of the Ln from an uranyl nitrate solution after hydrofluoric acid had been added and the solution percolated into a small alumina column. The retention of the lanthanides is quantitative and after elution with hot nitric acid the Ln are coprecipitated with  $\text{La}^{3+}$  carrier and spectrochemically analysed. Using this procedure [4] extremely small amounts of RE can be determined.

## Thorium Technology

A pilot plant is in operation for the purification of a thorium concentrate obtained from the industrialization of the monazite sand. The crude thorium sludge, containing thorium hydroxide and about 1% uranium, is treated with hot nitric acid and digested to precipitate the silica and then filtered. The nitrate solution, after addition of  $\text{NaNO}_3$  (2.2 M  $\text{NaNO}_3$  and 0.8 M  $\text{HNO}_3$ ), is purified by solvent extraction with 50% TBP-varsol. The final nuclear grade products in this unit are an aqueous solution of  $800 \text{ g l}^{-1}$   $\text{Th}(\text{NO}_3)_4$ , crystallized  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  and uranyl carbonate solution. This installation is capable of producing thorium oxalate and converting this salt into the oxide.

Thorium is stripped first with water and then uranium is recovered from the organic phase with carbonate, the treated clean solvent being recycled continuously.

A second raw material is thorium sulphate precipitated from the above-mentioned sludge. This concentrate is reasonably pure, virtually free from uranium, but still contains some lanthanides. Two procedures have been worked out: in the first the thorium sulphate is converted into thorium octo-carbonate ( $\text{ThOCO}_3$ ) which is filtered out and then dissolved with nitric acid, the final purification being made by TBP-varsol at the same pulsed columns pilot plant; in the second flowsheet the thorium sulphate is dissolved with water and loaded into a strong cation exchanger column so that the column is saturated with thorium, using the excellent affinity of  $\text{Th}^{4+}$  to the exchanger. Minor impurities like alkalis, alkaline earths, aluminium, iron and even rare earths are displaced. After washing the impurities and excess of thorium with water, the column is eluted with ammonium carbonate and the eluate converted into  $\text{ThOCO}_3$ ; this solid product is filtered out and finally dissolved with nitric acid and crystallized as  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ .

Some local non-nuclear uses for thorium are the industrial fabrication of gas lamp mantles (thoria-ceria) and an application in the preparation of several special ceramics, like  $\text{ThO}_2 \cdot \text{CaO}$  (5%) and  $\text{ThO}_2 \cdot \text{Y}_2\text{O}_3$  (8%).

### Radiothorium-228 Tracer

Mesothorium (radium-228) is collected from the effluents as  $\text{BaSO}_4$  ( $^{228}\text{Ra}$ , 5.7 y). A minor amount has been used for the preparation of a thorium-228 (1.9 y) tracer. This radioisotope is eluted from the  $\text{BaSO}_4$  with strong  $\text{HNO}_3$ . The elution can be done in the milking way, keeping the  $\text{BaSO}_4$  for some time in order to wait for the development of thorium-228. With this radio-tracer other interesting radioisotopes have been used, like radon-220 (55 s), lead-212 (10.6 h), bismuth-212 (60.6 min) and thallium-208

(3.1 min). Special interest is shown in  $^{208}\text{Tl}$  as a high gamma energy emitter (2.61 MeV) used for (gamma, n) reaction and deuterium analysis.

### Thorium Quality Control

Special care to obtain high purity thorium is shown in the determination of very small amounts of uranium and lanthanides. A very simple, highly sensitive and efficient technique for the direct determination of uranium in thorium is hanging mercury drop voltammetry. Uranium is determined in aqueous thorium nitrate or dissolved  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  directly, with no chemical separation, starting with a  $5 \text{ g l}^{-1}$  Th containing  $0.03 \mu\text{g ml}^{-1}$ , that is,  $0.3 \mu\text{g U}$  in the electrolytic cell. The method allows the determination of 6 ppm U in Th. A lower content requires previous concentration via solvent extraction of uranyl nitrate with 1% TBP-petroleum ether-EDTA- $\text{Al}(\text{NO}_3)_3$ , and stripping of U and final determination as mentioned. The peak potential of uranium in  $\text{H}_2\text{SO}_4$  as supporting electrolyte is 0.67 V SCE.

Lanthanides are determined after separation and concentrated into a cellulose column from 11%  $\text{HNO}_3$ -ether. In a typical analysis if 79 g  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  is percolated, only ca. 100 mg  $\text{ThO}_2$  remains in the column together with the RE after elution with 0.01 M  $\text{HNO}_3$  used as carrier for the precipitation of the oxalates. The oxides are mixed with AgCl carrier and analysed spectrochemically, the total of Eu, Gd, Sm, Dy, Yb, Y, Lu, Tm and Er being less than 1 ppm/ $\text{ThO}_2$ .

### Decontamination of Ln and Th from U

A very simple, efficient and easily applied method for the separation and concentration of extremely low lanthanide and thorium content from uranium has been developed and is used in several situations. The procedure is based on the retention of Th and Ln from solutions containing about 0.3 M HF when percolated through a small chromatographic alumina column. Rare earths and thorium are quantitatively sorbed onto the alumina and can be separated from dilute or concentrated ( $100\text{--}250 \text{ g l}^{-1}$  U) uranyl solutions. The retention mechanism is not well established and deserves more study.

This simple procedure can be applied to such separations as  $^{234}\text{Th}$  and  $^{230}\text{Th}$  from uranium. In the case of thorium-234, the column serves as an efficient milking cow for  $^{234}\text{Pa}$  (6.7 h) and  $^{234\text{m}}\text{Pa}$ , and the separation of fission rare earths. Alumina can also be used for the containment of such fission lanthanides for disposal. A limitation is the precipitation of thorium and lanthanides as fluorides, which starts from  $20 \text{ mg l}^{-1}$  of these elements and the precipitate appears after 20–30 min. In this case the controlled

addition of HF to an aliquot is recommended, followed by percolation to a second aliquot and then percolation and so on.

#### *Separation and Concentration of Plutonium*

The same procedure has proved very efficient for the retention and concentration of plutonium. Pu(III), Pu(IV) and Pu(IV) behave differently, the distribution coefficients (DF) being 2.8, 3.6 and 47.2, respectively. An experiment using 30 l of Pu(IV) in HNO<sub>3</sub> and 0.1 M HF showed a retention of 97% for Pu(IV) in a column of 10 ml Al<sub>2</sub>O<sub>3</sub>. Plutonium can be eluted with hot 3 M HNO<sub>3</sub>–0.005 M Fe<sup>2+</sup>. Experiments for retention and concentration of neptunium, which is also efficiently sorbed on alumina, are in progress.

#### **Fractionation of Rare Earth Elements**

IPEN has been very active in the fractionation of lanthanides. The raw material is the rare earth chlorides mixture, a natural mixture of all the lanthanides, produced by the industrial exploitation of monazite sand. The RECl<sub>3</sub> mixture is supplied by Nuclemon, São Paulo, a subsidiary of Nuclebrás.

The idea is first of all to remove cerium and then to apply some conventional techniques, such as double alkaline rare earth sulphates and controlled basic precipitation, especially to remove yttrium and lanthanum. The enriched fractions are sent to final refining using a strong cationic ion exchanger.

The removal of cerium has been carried out using alternative procedures for its selective oxidative precipitation. One such procedure is homogeneous precipitation with urea–H<sub>2</sub>O<sub>2</sub>. The optimal conditions are: initial RECl<sub>3</sub>, 35–70 g l<sup>-1</sup> R<sub>2</sub>O<sub>3</sub>, pH 2, (urea/R<sub>2</sub>O<sub>3</sub>) = 4, (H<sub>2</sub>O<sub>2</sub>/Ce<sub>2</sub>O<sub>3</sub>) = 1.5–5.0, hydrolysis at 88–90 °C. The Ce(IV) precipitate yield is over 90% with some heavy lanthanides coprecipitated. After leaching with 0.3–0.8 M HNO<sub>3</sub> the CeO<sub>2</sub> yield is 97–99%.

A second technique for the removal of cerium is the oxidation with air–NH<sub>3</sub> gas at 60 °C, which gives directly a fraction of CeO<sub>2</sub> > 95–97%. This precipitate after treatment with dilute HNO<sub>3</sub> produces a CeO<sub>2</sub> yield of >99%.

The low cerium fraction is again precipitated by the hydrolysis of urea in three fractions rich in Nd, Pr and Sm, and the final filtrate is a lanthanum concentrate. Each fraction is refined using the cation exchanger technique for the production of four fractions of Nd (99%), Pr (99%), La (99%) and Sm (90% pure). The lanthanides are eluted by EDTA–HAc using a concentration gradient technique.

After using the technique of two columns for several years, the first one in the Cu<sup>2+</sup> form, frac-

tionation today is optimized in such a way that a retention cation like Cu<sup>2+</sup> or Zn<sup>2+</sup> is no longer used. The elution is optimized exploring the gradient technique for EDTA–HAc concentration and pH of eluent; very pure individual lanthanides are produced in this way.

The use of solvent extraction for the separation of lanthanides in the direct fractionation of natural RECl<sub>3</sub> with 20% EHPA–dodecane, (O/A) = 2.5, in one stage, results in an extraction of about 10% of the total Ln with an enrichment factor of 10–15 for Eu, Gd, Tb and Y, those lanthanides being extracted at a ratio of 90–99%. After being stripped from the organic phase, the final refining is done by cation ion exchange.

#### **Applications**

Examples of home demand for rare earths are: Gd for studying UO<sub>2</sub>–Gd<sub>2</sub>O<sub>3</sub> pellets; Ce for shielding glass; dysprosium and thulium for the manufacture of thermoluminescent dosimeters based on CaSO<sub>4</sub>·Dy and CaSO<sub>4</sub>·Tm.

#### **Rare Earth Analytical Chemistry**

The main progress in rare earth analytical chemistry will be briefly mentioned here. There is no one analytical procedure capable of solving all the problems and for this reason several analytical techniques have been used in combination with each other to cope with common and special problems. Atomic absorption (AA), graphite furnace atomic absorption (GFAA), spectrography, X-rays, neutron activation analyses, spectrofluorimetry, UV–Vis spectrophotometry, and voltammetry have been used for major and minor RE determinations.

Spectrochemical determinations of Ln have been made directly on the oxides using a special chamber with a mixture of 80% argon–20% oxygen, and for traces lanthanum has been used as carrier.

As mentioned before, especially for the determination of extremely low amounts of Ln in uranium, a previous separation using the Al<sub>2</sub>O<sub>3</sub>–HF system is of very practical importance, followed by the determination using spectrochemical, GFAA, AA, spectrofluorimetry, or voltammetry. By this last technique Eu and Yb have been determined using 0.1 M NH<sub>4</sub>Cl or EDTA as a support electrolyte. The peak potentials for both are easily distinguished,  $E_p(\text{Eu}^{3+}) = -0.66$  V SCE and  $E_p(\text{Yb}^{3+}) = 0.42$  V SCE with 0.1 M NH<sub>4</sub>Cl at pH 2–6 as support electrolyte. To follow the Ln elution using EDTA as eluent, the

TABLE I. Experimental Conditions for Direct Spectrofluorimetric Determination of Rare Earths in Inorganic Acids and Thorium Solutions

RE	Excitation (nm)	Fluorescence (nm)	Detection limit in	
			HCl ( $\mu\text{g/ml}$ )	ThCl <sub>4</sub> ( $\mu\text{g RE/g Th}$ )
Ce	257	350	0.002	0.01
Tb	352 (372)	545	0.5	50
Eu	394	595	10	80
Pr	222 <sup>a</sup>	478	0.5	n.f.
Dy	352	480	100	n.f.
Gd	275	312	100	n.f.

<sup>a</sup>Excitation peak completely absorbed by Th.  
n.f. = does not fluoresce.

TABLE II. Lanthanide Spectrofluorimetric Determination in Uranium

Detection limit for Ln by fluorescence ( $\mu\text{g Ln/100 mg Y}$ )		
Ln	Y <sub>2</sub> O <sub>3</sub>	YVO <sub>4</sub>
La	n.f.	n.f.
Ce	n.f.	n.f.
Pr	10	n.f.
Nd	IR	IR
Sm	30	0.02
Eu	0.4	0.02
Gd	40	n.f.
Tb	0.01	n.f.
Dy	4	0.01
Ho	4	2
Er	4	0.5
Tm	10	0.2
Yb	IR	IR
Lu	n.f.	n.f.

n.f. = does not fluoresce. IR = infrared.

voltammetric technique is particularly useful, Eu<sup>3+</sup> being measured directly with no chemical separation. The  $E_p(\text{Eu}^{3+})$  in 0.1 M EDTA at pH 6–13 is 1.30 V SCE and the sensitivity is considerably greater,  $1 \times 10^{-6}$  M Eu<sup>3+</sup> ( $1.0 \mu\text{g ml}^{-1}$  Eu in the cell), compared with conventional polarography ( $2 \times 10^{-3}$  M Eu<sup>3+</sup>). For NH<sub>4</sub>Cl as support electrolyte, a sensitivity of  $3 \times 10^{-7}$  M ( $0.3 \mu\text{g ml}^{-1}$  Eu in the cell) can be determined. There is no interference of other Ln so Eu can be measured directly in any mixture of rare earths.

The determination of cerium as a following up element for the control of purification of uranium is easily done by spectrofluorimetry after collection and enrichment into alumina. After eluting the Ln with hot HCl or HClO<sub>4</sub>, Ce is determined directly in the acid solution;  $0.002 \mu\text{g Ce/g U}$  can be measured. The determination of Ce directly in thorium can effectively be done in HCl or HClO<sub>4</sub> solution,  $0.004 \mu\text{g Ce ml}^{-1}$  of a  $200 \text{ g Th l}^{-1}$ , that is,  $0.02 \mu\text{g Ce/g Th}$  being analysed without problem (excitation at 257 nm and emission at 350 nm). In the same thorium solution some rare earths can be measured together with cerium, as can be seen in Table I.

A more elaborate and time-consuming technique, solid-state spectrofluorimetry, is of very high sensitivity. In YVO<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> matrices Dy, Eu, Sm, Tm, Er and Ho can be determined very efficiently, as is shown in Table II.

Finally, spectrofluorescence studies for the determination of lanthanides in HCl and K<sub>2</sub>CO<sub>3</sub> solutions are mentioned. The fluorescence of Ln in K<sub>2</sub>CO<sub>3</sub> is considerably more sensitive than in acid solutions. By this technique Sm, Eu, Gd, Tb, Dy and Tm (see Table III) can be determined. Figure 1 depicts the emission fluorescence spectra for some rare earths in K<sub>2</sub>CO<sub>3</sub> and HCl solutions. The procedure has been used routinely for the immediate control of the fractionation of individual rare earth elements.

TABLE III. Fluorescence Characteristics of Lanthanides in 3 M Potassium Carbonate Solution

Ln	Excitation* (nm)	Fluorescence* (nm)	Limits		$\sigma$ (%)
			Detection ( $\mu\text{g/ml}$ )	Determination (mg/ml)	
Sm	406, 380	596, 554	400	n.d.	
Eu	270, 396, 460	614, 590	0.5	$0.5 \pm 0.02^a$	4
Gd <sup>c</sup>	274	310	5.0	$4.8 \pm 0.3^a$	6
Tb	240, 280	542, 490	0.1	$0.09 \pm 0.01^a$	11
				$0.10 \pm 0.02$	20
Dy	350, 328, 388, 294	480, 576	10	$10 \pm 1$	10
				$11 \pm 2^b$	18
Tm	360	450	50	$48 \pm 7^a$	14

\*Peaks of decrescent intensity. <sup>a</sup>Calibration curve method; <sup>b</sup>standard addition method; <sup>c</sup>0.6 M K<sub>2</sub>CO<sub>3</sub>. n.d. = not determined. Seven determinations were made for each lanthanide.

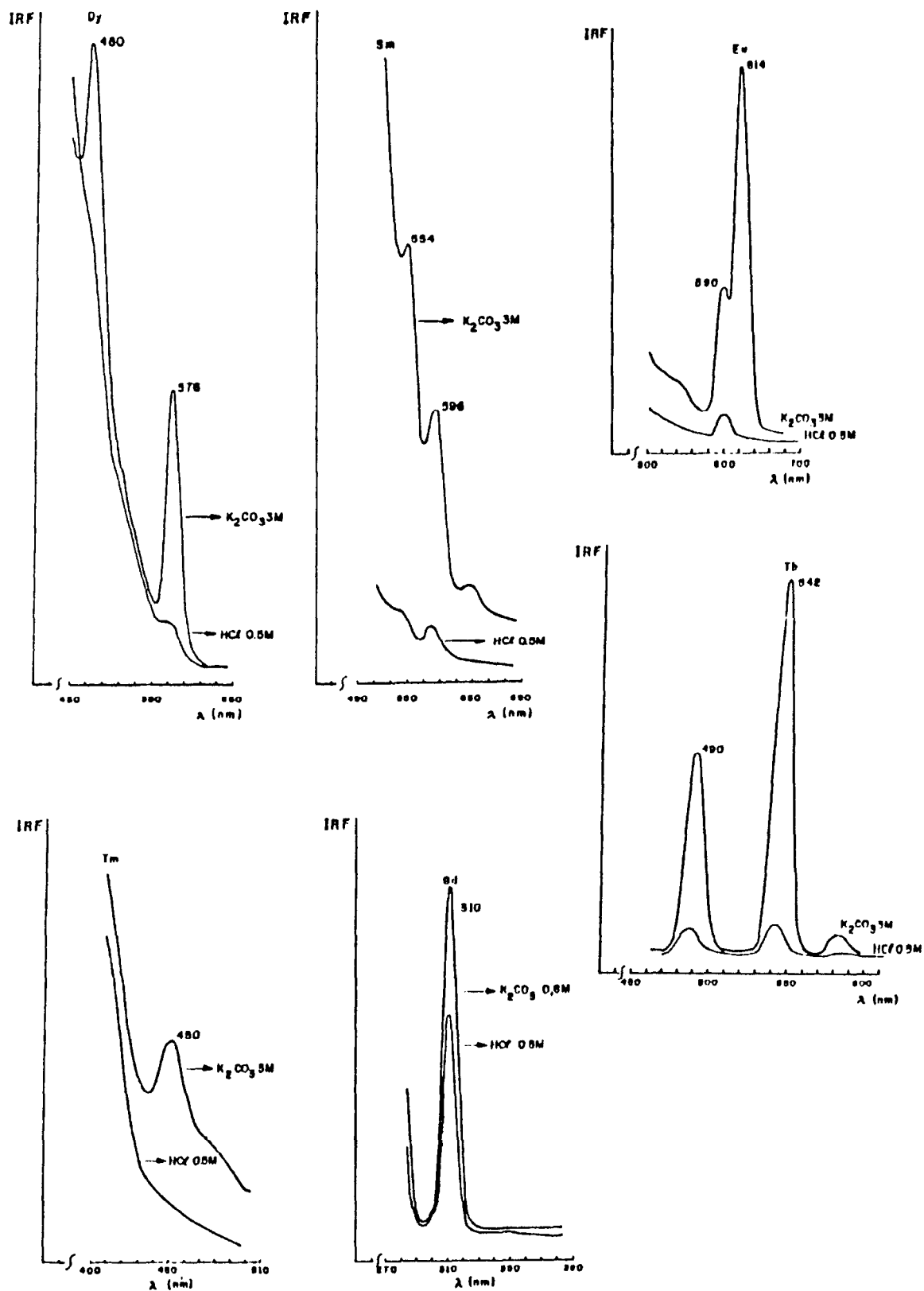


Fig. 1. Emission fluorescence spectra of Dy ( $100 \mu\text{g ml}^{-1}$ ), Sm ( $1 \text{ mg ml}^{-1}$ ), Eu ( $200 \mu\text{g ml}^{-1}$ ), Tm ( $600 \mu\text{g ml}^{-1}$ ), Gd ( $200 \mu\text{g ml}^{-1}$ ) and Tb ( $100 \mu\text{g ml}^{-1}$ ) in 0.5 M HCl and 3.0 M  $K_2CO_3$ .

## References

- 1 K. Brill and P. Krumholz, 'Produção de Óxido de Tório Nuclearmente Puro', Instituto de Energia Atômica, São Paulo, 1965 (IEA-115).
- 2 P. Krumholz and F. Gottenker, 'Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 8 August–20 August 1955', Vols. 4–8: 'Production Technology of the Material Used for Nuclear Energy', United Nations, New York, 1956, p. 126–128.
- 3 J. M. França Jr., 'Usina Piloto de Purificação de Urânio Pelo Processo de Colunas Pulsadas em Operação no Instituto de Energia Atômica', Instituto de Energia Atômica, São Paulo, 1972 (IEA-277).
- 4 A. Abrão, 'Chromatographic Separation and Concentration of Thorium and Rare Earths from Uranium Using Alumina-Hydrofluoric Acid. Preparation of Carrier-free Radiothorium and Contribution to the Fission Rare Earths', Instituto de Energia Atômica, São Paulo, 1970 (IEA-217).