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SUMMARY

This paper describes the determination of vanishing small amounts of rare earths in uranium by fluorescence spectrometry. The rare earth elements are separated and concentrated onto a small alumina (3 ml Al_2O_3) column after percolation of $UO_2(NO_3)_2$ - 0.3 M HF solution whose concentration can be as high as 250 g U/Litter. Thorium, if present, is also retained by the alumina. The rare Earth group and thorium are eluted with hot 1 M HCl or 1 M $HClO_4$.

The eluted lanthanides are determined using solid matrix. Dy, Eu, Sm, Tm, Er and Ho are excited into an YVO_4 matrix, and Tb, Pr and Gd are excited into an Y_2O_3 matrix. Although the first six elements also fluoresce into an Y_2O_3 matrix, their fluorescence is considerably higher into YVO_4. Cerium, that does not fluoresce either into YVO_4 or into Y_2O_3, is determined directly in the eluate. Ce-III is highly fluorescent in dilute inorganic acids and can be determined at concentration as low as 0.001 μg/ml.

Nd and Yb when into Y_2O_3 matrix fluoresce as well, but their fluorescence band is in the infrared region (800-1000 mμ) and were not determined here. La and Lu are not fluorescent at all into the used matrices.

The procedure has been applied to the determination of rare earths in 20 grams samples of uranium and its compounds. The lower concentration of rare earth elements analysed in uranium was (μg of lanthanide/g U): Dy-0.0005, Eu-0.001, Sm-0.001, Tm-0.0005, Er-0.02 and Ho-0.1, into YVO_4 matrix, and Tb-0.005, Pr-0.5, Gd-2.0 into Y_2O_3 matrix; Ce-0.002, directly in HCl or $HClO_4$ solution.

INTRODUCTION

The determination of microquantities of lanthanides and its compounds is a difficult task and a challenge to the analyst. Rare Earths (RE) as impurities are of great concern chiefly in materials for nuclear energy interest, mainly in uranium and thorium. The lanthanides occur in all uranium and thorium raw materials and must be removed to a level of only a few parts per million to minimize their effects as neutron absorbers. The importance of its determination is chiefly concerned to the neutron economy when the uranium is destinate to be used as fuel element. In this case the RE content must be rigorously controlled since, as it is well known/1/, some of them (Sm, Dy, Gd, Eu, Er) have high cross section for thermal neutron and could interfere seriously in the neutron economy of the reactor.

The occurrence of RE at extremely low concentration in uranium and thorium is responsible for the search and development of quite elaborate procedures for its detection, separation, concentration and determination, as a group or individually. Frequently the RE are present in products like uranium and thorium as a mixture of all RE elements.

Procedures for determination of macro amounts of RE are reasonably direct and realiable. Its quantitative determination is, in the general case, a double task of determining the total RE content and determining the individual RE of more interest. Determination of total

RE is based of chemical methods that exploit the similar behavior of these elements, such as oxalate precipitation and volumetric titration with complexing agents like EDTA.

While the macrodetermination of total RE is rather simple, its determination at trace level in matrices like uranium and thorium is a difficult problem to be solved. More, the estimation of the individual elements in the RE mixture is quite difficult and depends on physical measurements using properties such as electronic spectra and x-ray fluorescence spectra, both being most useful for macro amounts. On the other hand, emission spectra can be used for macro and micro levels. Emission spectrography has been applied to the direct determination of traces amounts of RE impurities in pure RE matrices and to the determination of trace amounts of RE in uranium/2/ and thorium after preliminary isolation. Activation analysis is another technique that could be applied for some of the RE elements.

The direct determination of microquantities of RE in materials such as U, Th and Zr is not possible even using the most powerful techniques like emission spectrochemical analysis, activation analysis and atomic absorption spectroscopy; this determination usually requires preliminary chemical separation and concentration. Because of the great chemical similarity of the individual RE and yttrium with one another, the determination of an individual element in the group is very difficult and rather impossible by chemical methods, except for cerium and europium.

In this paper a method is outlined by a suitable combination of chromatographic separation of traces of RE from uranium on an alumina column and the spectrofluorimetric determination of individual RE. It is a contribution to the RE chemistry at extremely low concentration, specially to its separation from uranium as a group and its individual determination by spectrofluorimetry. The proposed method allows the determination of Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm.

EXISTING METHODS FOR SEPARATION AND CONCENTRATION OF RE FROM URANIUM

The most frequently outlined methods for the separation of Th and RE from U for analytical purpose include precipitation (co-precipitation with carriers), solvent extraction, ion exchange and other chromatographic methods. One of the most widely used technique for the separation of Th and RE from U is the prior solvent extraction of uranyl nitrate with TBP-diluent/3,4,5/, being those elements collected from the raffinate with use of non-isotopic or isotopic carriers. A brief revision of methods for the separation of Th and RE from uranium is given by Abrão/6/. One of the disadvantages of existing methods pointed out in that paper is the separation of the major constituent (uranium).

Chromatographic separation on cellulose column has been used for the separation of thorium from uranium in HNO_3 ether medium/7,8,9/ and of RE from uranium/10,11/.

PROPOSED METHOD FOR SEPARATION OF RE FROM U AND ITS INDIVIDUALLY DETERMINATION

The separation and concentration of extremely low amounts of RE from U, as a group, is achieved by the technique published by Abrão/6/. The method is simple and efficient and is based upon the sorption of RE elements on an alumina column from uranyl nitrate 0.3 M in HF. The method allows complete separation from uranium and the great majority of all commonly associated elements, except thorium, that is also retained on the alumina. The elution of RE and Th from Al_2O_3 was somewhat ameliorated by introducing the calcination of alumina at 900°C during one hour prior the percolation step. This modification of the original methods/6/ allowed a complete elution of RE and Th with small volume of hot 1 M HCl percolated directly on the column.

After elution of RE and Th the lanthanides are determined individually by spectrofluorimetric technique. Cerium is the only element determined directly in the HCl solution. For the determination of other RE, yttrium was added to the eluate to act as the matrix, the RE group precipitated as oxalate and ignited to Y_2O_3. Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm fluoresce directly in the yttrium oxide matrix. Sm, Eu, Dy, Ho, Er and Tm fluoresce in the Y_2O_3 after addition of sodium vanadate and new ignition. Dy, Eu, Sm, Ho, Er and Tm are determined in YVO_4 matrix and Tb, Pr, Gd are determined in Y_2O_3 matrix.

To achieve this goal a prior study of the conditions for the fluorescence of RE in solution and in solid matrices was performed and will be described here.

FLUORIMETRIC DETERMINATION OF RE IN SOLUTION

In a previous paper/12/ the fluorescence spectra of Ce, Eu, Tb, Dy, and Gd in pure inorganic acid solutions and its determination in thorium solution was studied. The direct spectrofluorimetric determination of Ce, Eu and Tb in highly pure thorium chloride was accomplished. While specially Ce is easily detected and determined due to its highly intense fluorescence, the detection limits for Tb and Eu in pure HCl are only 0.5 and 10 μg/ml, respectively, as can be seen in Table I.

TABLE I

Experimental Conditions for Direct Spectrofluorimetric Determination of RE in Inorganic Acids and Thorium Solutions /12/.

El.	Excit. (mμ)	Fluorescence (mμ)	Detection Limit in HCl (μg/ml)	Detection Limit in $ThCl_4$ (μg El/g Th)
Ce	257	350	0.002	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 fluoresce

* excitation peak completely absorbed by Th

To increase the sensitivity of fluorescence of other RE in solution the addition of such ions like tungstate/13,14/ and oxalate/15/ or some organic chelating agents like thenoyl Trifluoroacetone (TTA) and other betadicetones is recommended.

With exception of Ce, for the determination of traces amounts of RE in nuclear grade amonium diuranate and uranium oxides, the sensitivity of RE in solutions are not high enough and on the other hand, is not possible the determination of various RE at the same time.

This is the reason why we decided to study the determination of RE in solid matrices like Y_2O_3 and YVO_4, where the sensitivity is much higher.

FLUORIMETRIC DETERMINATION OF RE IN SOLID MATRICES

Only a few papers are published covering the RE determination by fluorimetry in solid matrices which use the so named crystallophosphors or luminophorscrystals. For the preparation of such compounds, alkalineearth sulfates/16/, fluorides/17,18/ tungstates/19,20/ vanadates/17,21-26/ and several oxides/27-31/ are mentioned. Due to its close similarity to the other RE, yttrium is a convenient element to be used with twofold task of carrier and Y_2O_3 matrix. The Y_2O_3 contributes to the formation of luminescent centers between yttrium oxide and the other rare earths oxides, so having the scope of an activator/32-36/. Some RE were detected as impurities in Y_2O_3 by their fluorescence in this matrix/27,37/. Ozawa et al/27/ used this property for the determination of Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm as impurities in Y_2O_3; 0.01 to 10 μg RE/g Y could be detected. Nd and Yb also fluoresce in this Y_2O_3 matrix/32/ but their fluorescence are in the infrared region and require a spectrofluorimeter sensible in this region.

The addition of vanadate ion to the yttrium for the formation of an Y_2O_3 - YVO_4 matrix allows the detection and determination of some RE in levels as low as 0.001 ppm RE/Y/24. Anikina et al/23/ used the intense fluorescence of some RE in YVO_4 and determined Gd, Eu and Sm in uranium metal using prior separation with the aid of cationic ion exchanger.

Although uranium in some cases can be used as a fluorescence activator for some RE, in a general way this element causes a total quenching of fluorescence of RE when in macroscopic concentration.

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 quartz cell (101-QS).

REAGENTS

All the RE solutions were prepared by dissolution of specpure oxides/12/ with high quality inorganic acids.

Uranyl nitrate solution was prepared by dissolution of U_3O_8 proceeding from the ignition of nuclear grade ammonium diuranate purified by TBP-varsol-HNO_3 system at IEA Pilot Plant.

Alumina (Chromatographic grade Merck) was previously ignited at 900°C during one hour. The column and its reservoir are depicted by fig. 1.

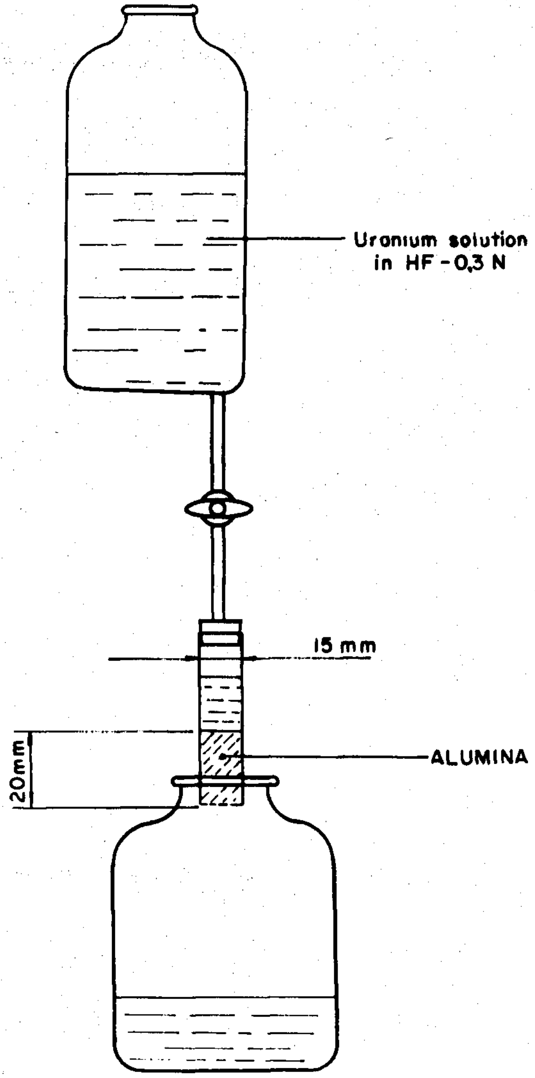

Fig. 1 - Apparatus used in the separation lanthanides-uranium.

CHARACTERISTIC FLUORESCENCE AND EMISSION SPECTRA OF RE IN Y_2O_3 MATRIX

The fluorescence and emission spectra of all rare earths elements were recorded in Y_2O_3 matrix. For each RE element 10 μg are added to 100 mg of Y, the oxalate precipited with 5 ml of 10% oxalic acid, filtered (paper) dried at 110°C and ignited (porcelain crucible) to oxide at 900°C during 1 hour and transferred to the support. La, Ce and Lu do not fluoresce in the Y_2O_3 matrix, while Nd and Yb fluoresce only in the infrared region and were not measured. The other RE and their characteristic peaks are shown in Table II.

TABLE II

Fluorescence Spectra Characteristics of RE determined in this paper.

	Y_2O_3 matrix		YVO_4 matrix	
El.	Excit.	fluoresc.*	Excit.	fluoresc.*
La	does not fluoresce		does not fluoresce	
Ce	does not fluoresce		does not fluoresce	
Pr	288	$\underline{632}$,618	does not fluoresce	
Nd	—	Infrared	—	Infrared
Sm	236	$\underline{565.5}$	320	603; 565; $\underline{647}$**
Eu	253	$\underline{612}$; 585	320	$\underline{620}$; 616; 596
Gd	276	$\underline{316}$	does not fluoresce	
Tb	306	544.5; 493	does not fluoresce	
Dy	351	$\underline{573}$	320	$\underline{575.5}$; 484.5
Ho	449	$\underline{551}$	320	$\underline{542}$; 546.5
Er	380	$\underline{564}$; 554; 540	320	$\underline{554.5}$; 526; 546.5
Tm	362	$\underline{454}$	320	$\underline{477}$
Yb	—	Infrared	—	Infrared
Lu	does not fluoresce		does not fluoresce	

* Decreasing intensity fluorescence peak

** Lower intensity but more free from interferences

— Used peak for determination.

The correspondent fluorescence and emission spectra recorded using the Al_2O_3 matrix are depicted for Tb, Eu, Pr, Ho, Dy, Er, Tm, Sm and Gd in figures 2 to 10, respectively.

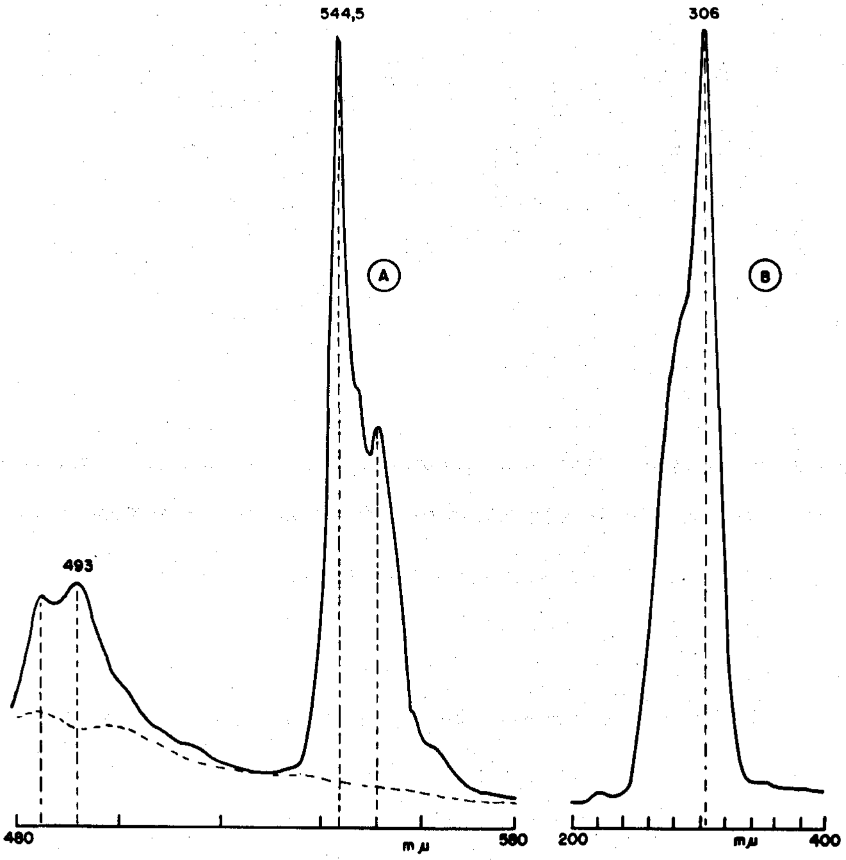

Fig. 2 - Emission (A) and excitation (B) spectra of Tb in Y_2O_3.
Tb = 10 μg
Y = 100 mg

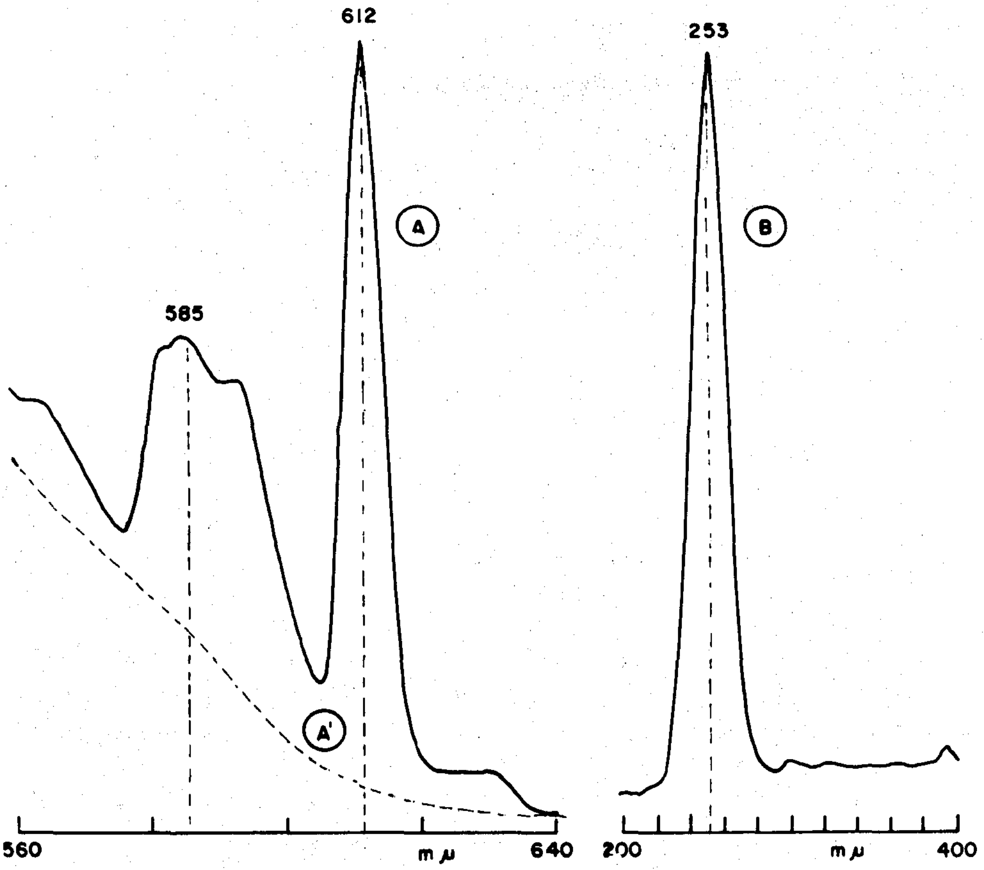

Fig. 3 - Emission (A) and excitation (B) spectra of Eu in Y_2O_3.
Eu = 10 μg
Y = 100 mg

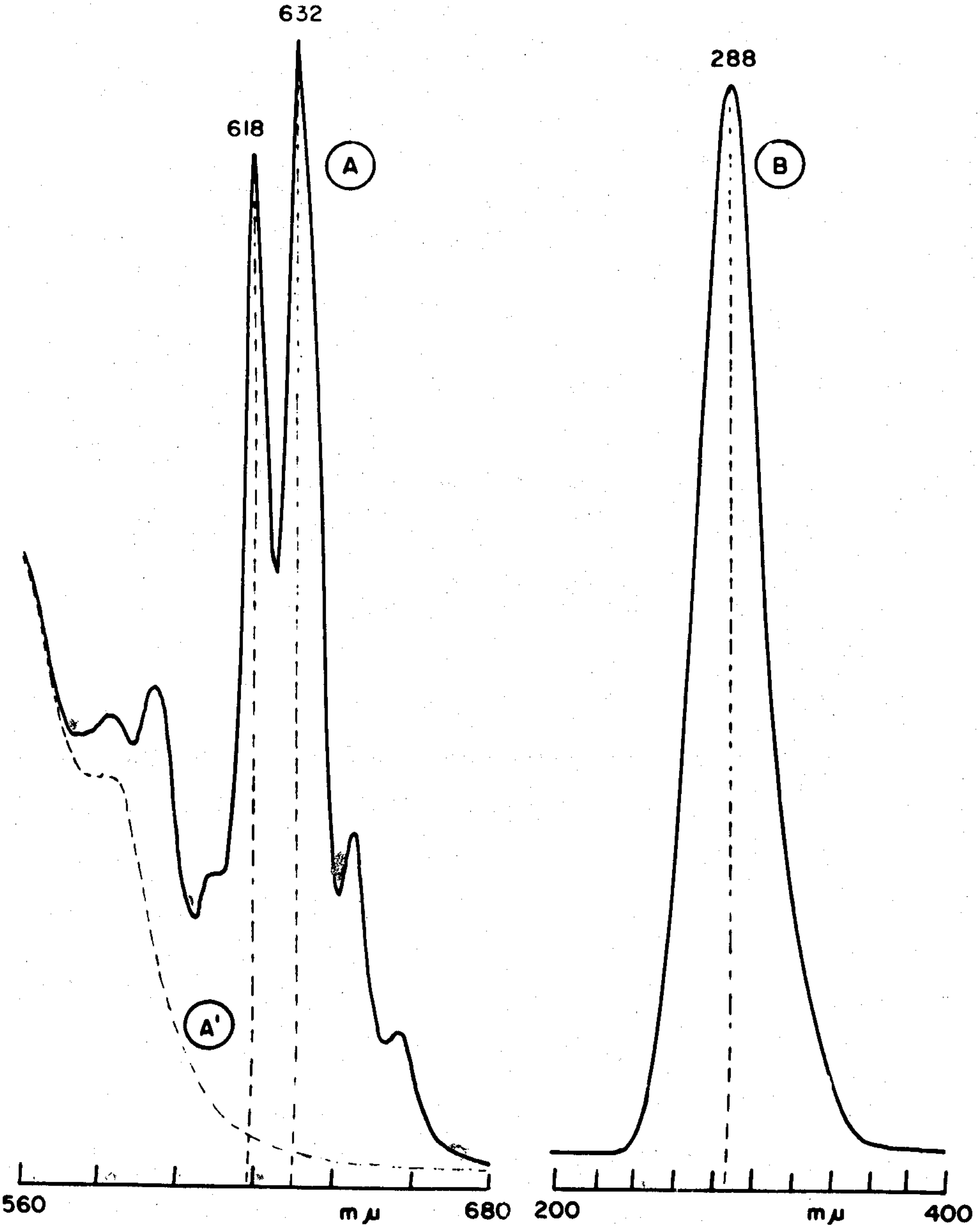

Fig. 4 - Emission (A) and excitation (B) spectra of Pr in Y_2O_3.
Pr = 100 μg
Y = 100 mg

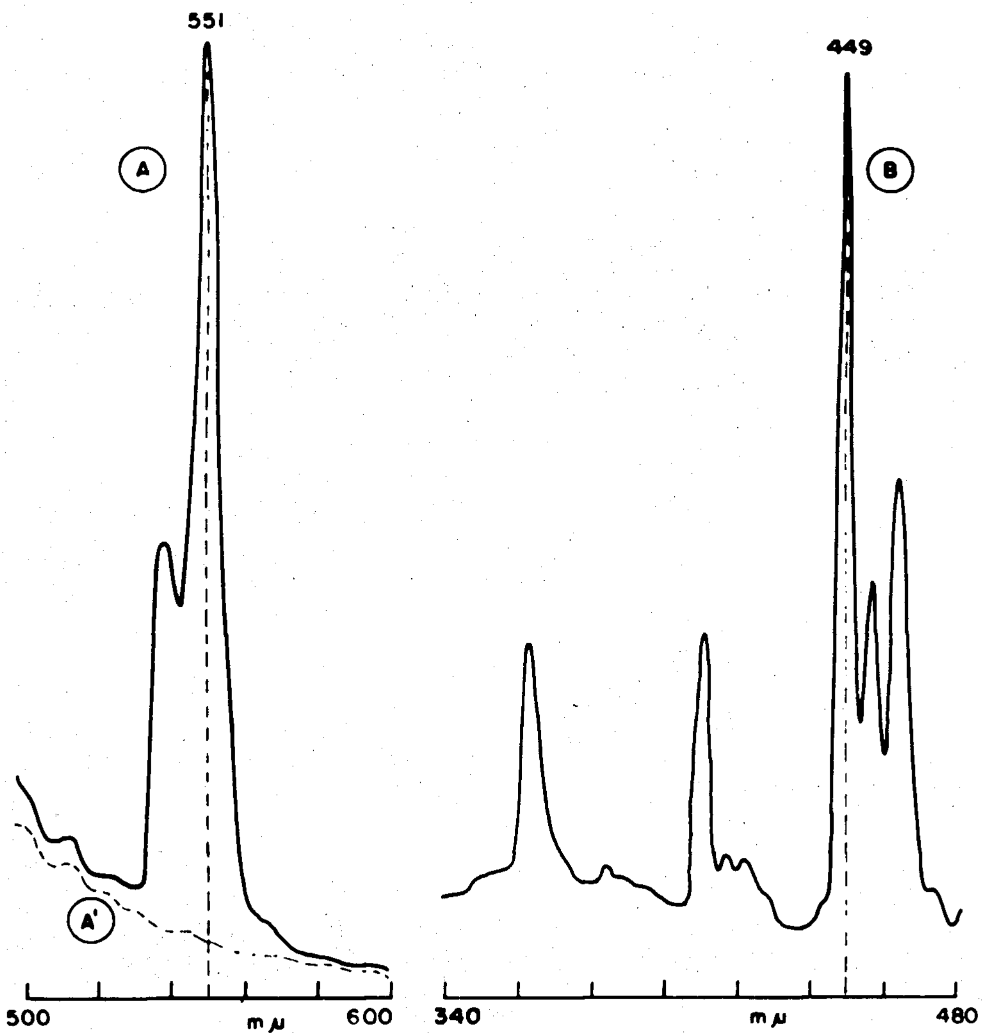

Fig. 5 - Emission (A) and excitation (B) spectra of Ho in Y_2O_3.
Ho = 50 μg
Y = 100 mg

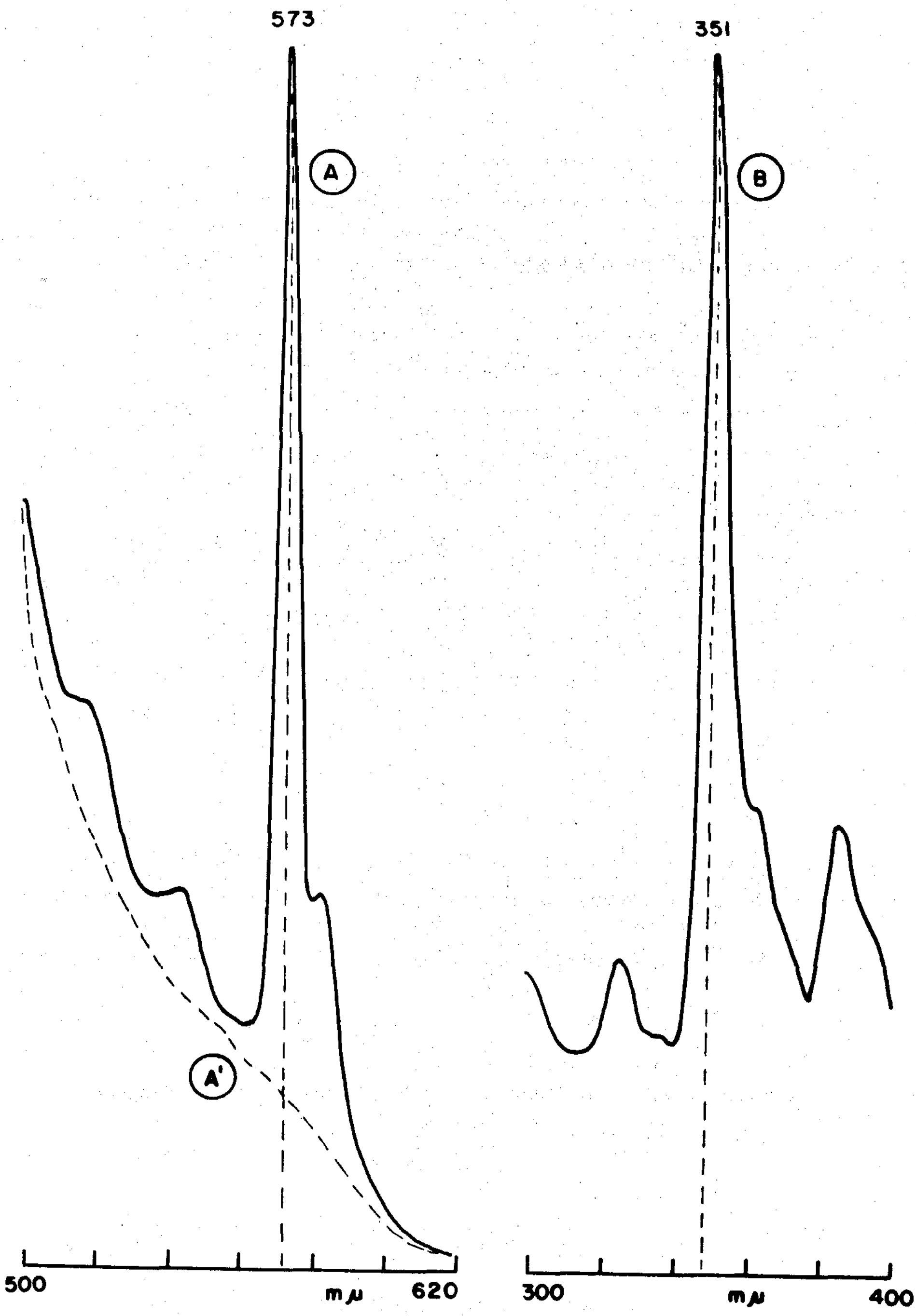

Fig. 6 - Emission (A) and excitation (B) spectra of Dy in Y_2O_3.
Dy = 100 μg
Y = 100 mg

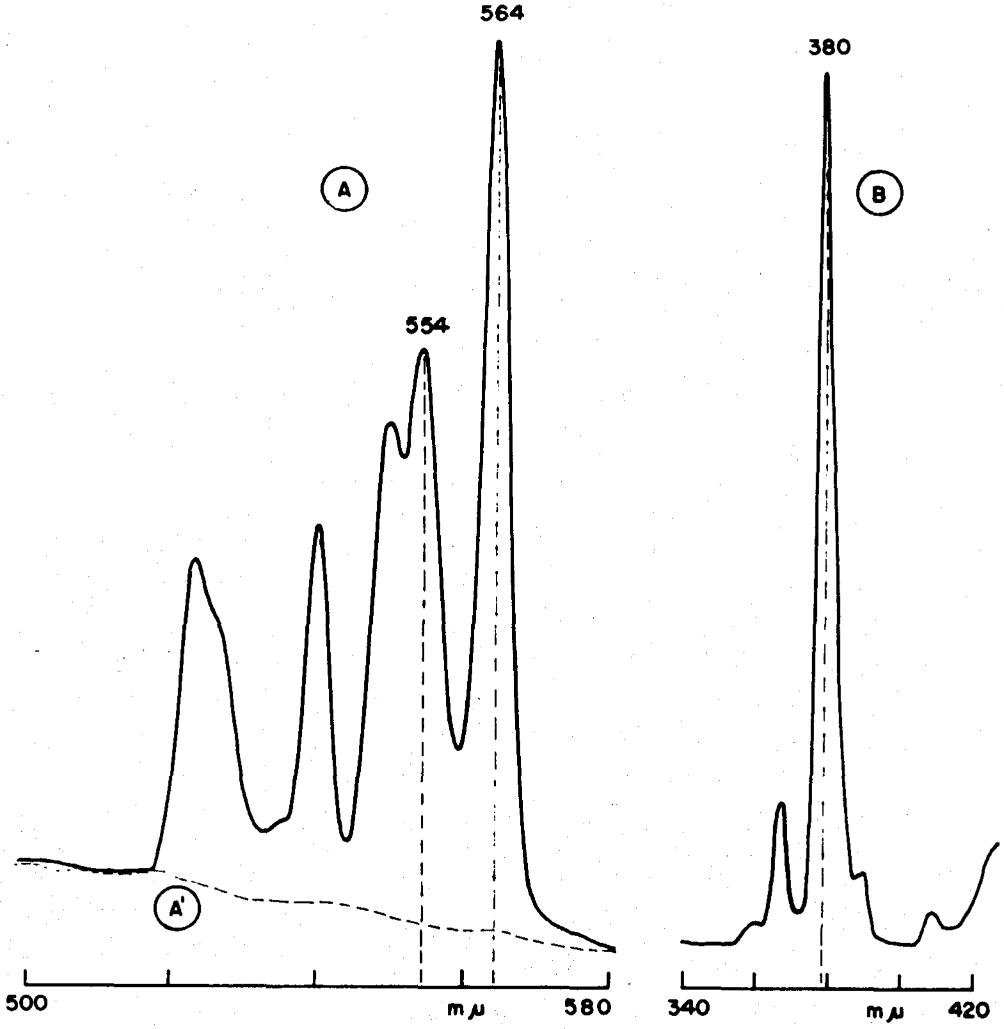

Fig. 7 - Emission (A) and excitation (B) spectra of Er in Y_2O_3.
Er = 50 µg
Y = 100 mg

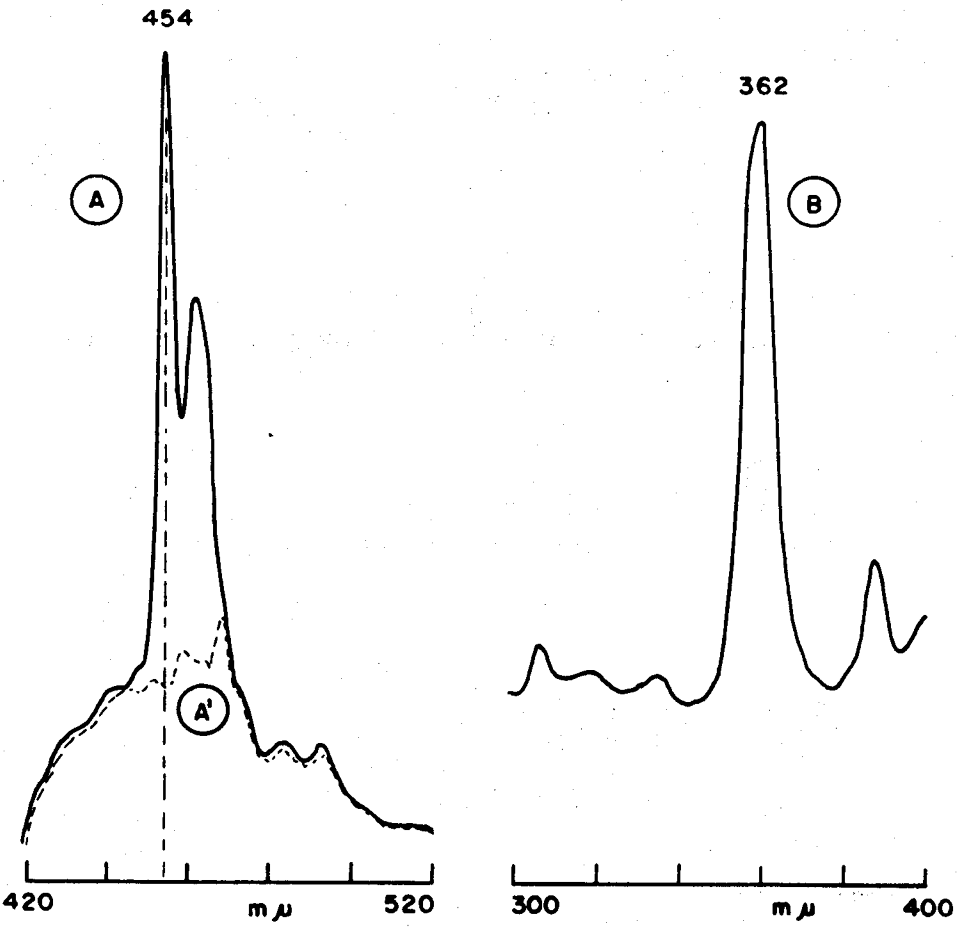

Fig. 8 - Emission (A) and excitation (B) spectra of Tm in Y_2O_3.
Tm = 50 μg
Y = 100 mg

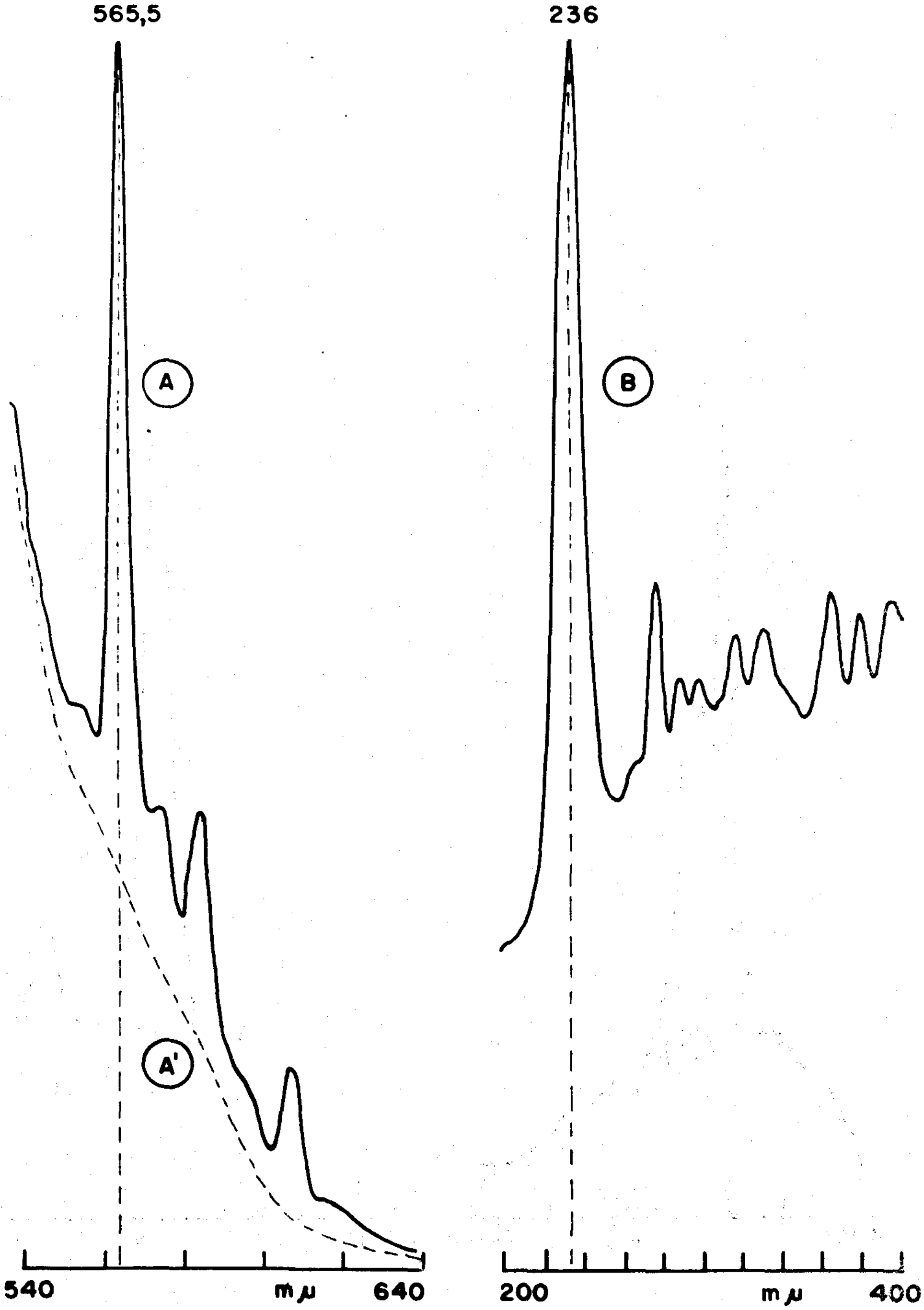

Fig. 9 - Emission (A) and excitation (B) spectra of Sm in Y_2O_3.
Sm = 50 μg
Y = 100 mg

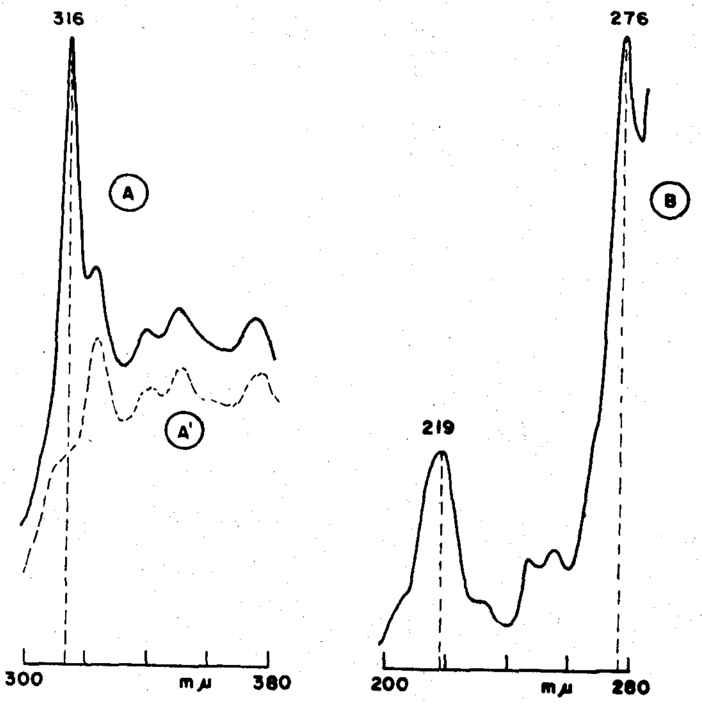

Fig. 10 - Emission (A) and excitation (B) spectra of Gd in Y_2O_3.
Gd = 100 μg
Y = 100 mg

CHARACTERISTIC FLUORESCENCE AND EMISSION SPECTRA OF RE IN YVO_4 MATRIX

The fluorescence and emission spectra of all RE elements were recorded in YVO_4 matrix. For each RE 1 to 50 μg of each element was added to 100 mg of Y and the Y_2O_3 oxide obtained as described before, but now using platinium crucible, since porcelain is attacked by the next YVO_4 preparation. To the cooled Y_2O_3, in the same crucible, 75 mg of NH_4VO_3 and 3 mg of $NaNO_3$ (0.3 ml of 1% solution) are added, the mixture dried and again ignited to 1000°C during 1 hour, cooled and transferred to the support and the fluorescence spectra recorded. La, Ce, Pr, Gd, Tb and Lu do not fluoresce, Nd and Yb fluoresce only in the infrared region. The characteristic values for the most intense peaks are in Table II and the correspondent fluorescence and emission spectra are depicted for Dy, Eu, Sm, Er, Tm, Ho in figures 11 to 16, respectively.

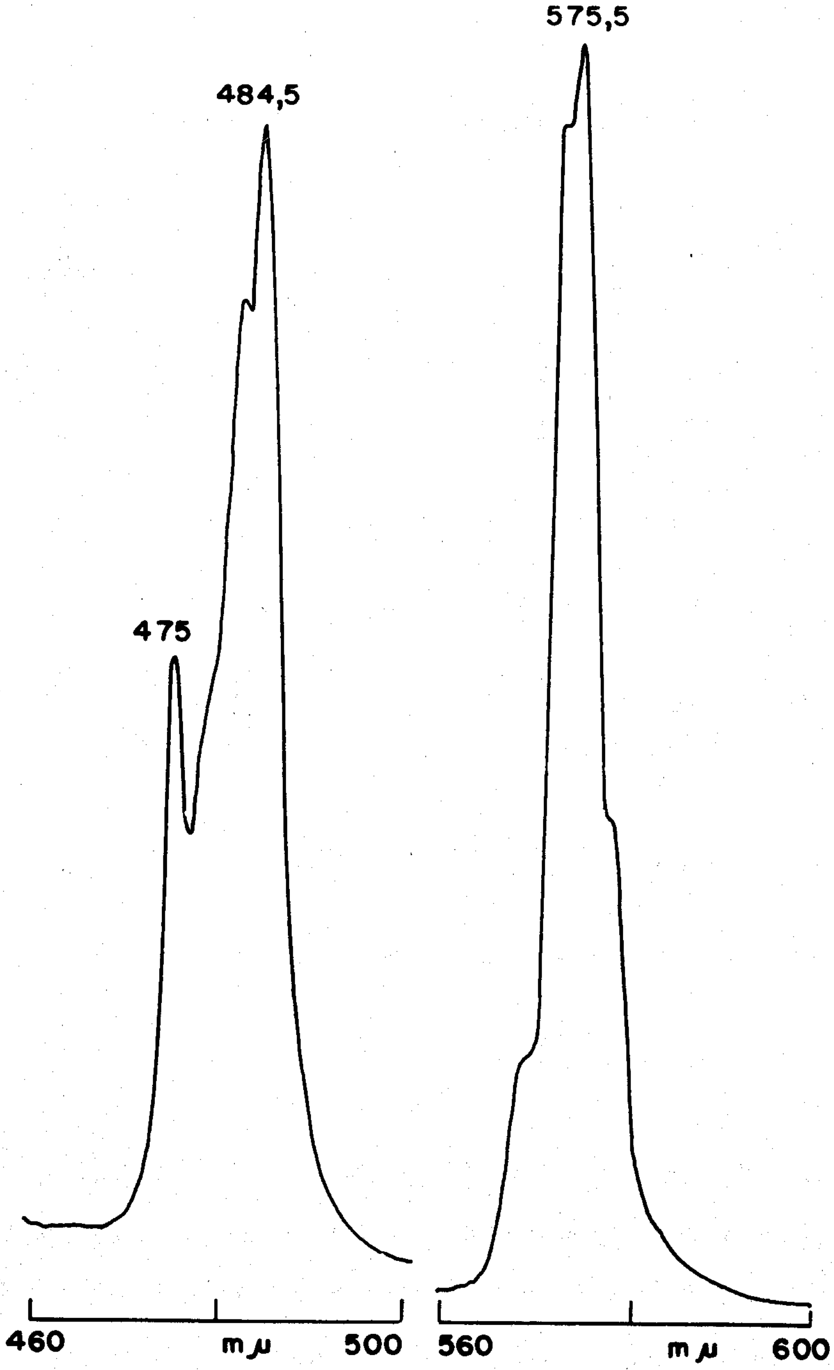

Fig. 11 - Emission spectrum of Dy in YVO_4.
Dy = 50 μg
Y = 100 mg
λe = 320 mμ

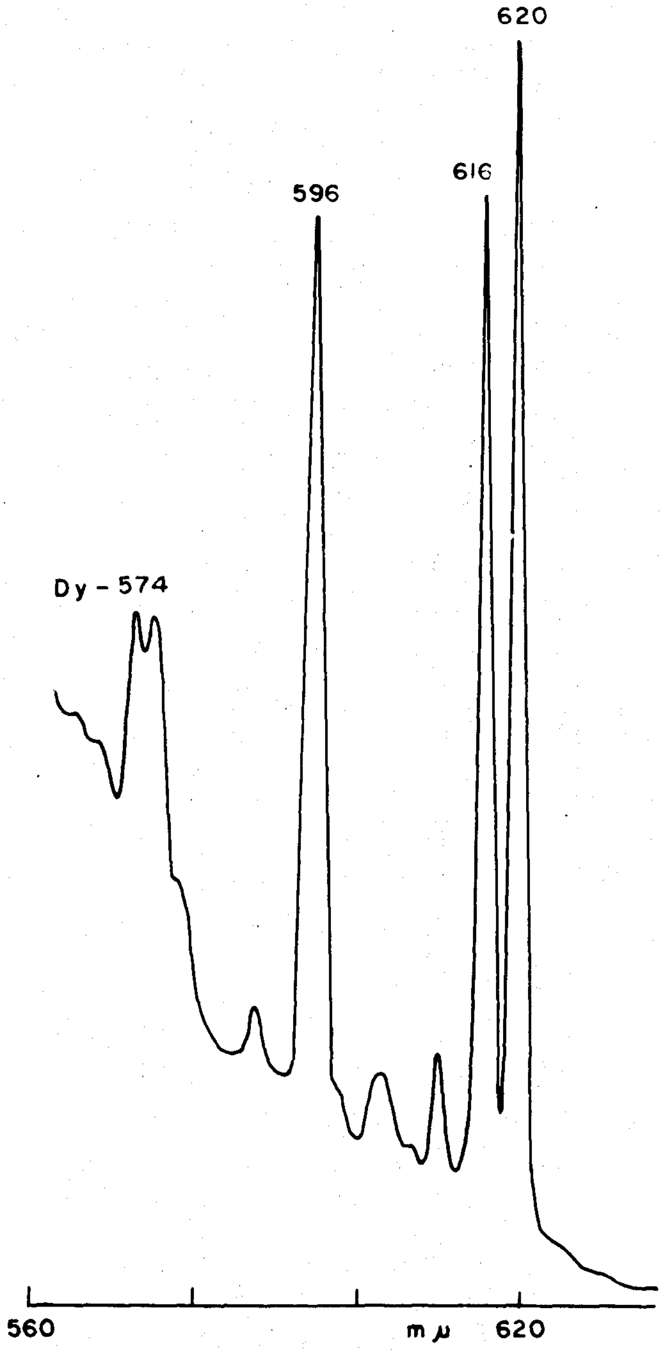

Fig. 12 - Emission spectrum of Eu in YVO_4.
Eu = 1 µg
Y = 100 mg
λe = 320 mµ

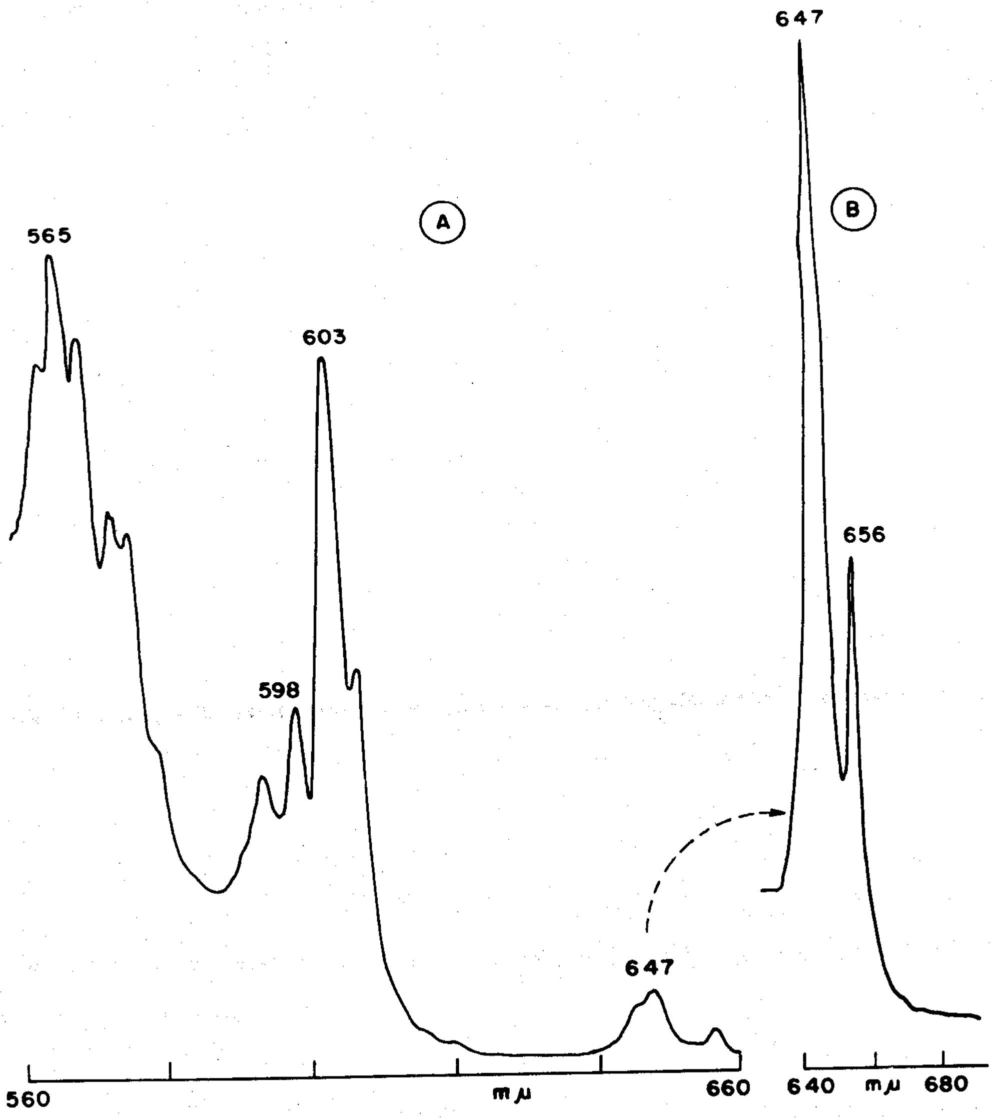

Fig. 13 - Emission spectrum of Sm in YVO_4.

Sm = 1 μg

Y = 100 mg

λe = 320 mμ

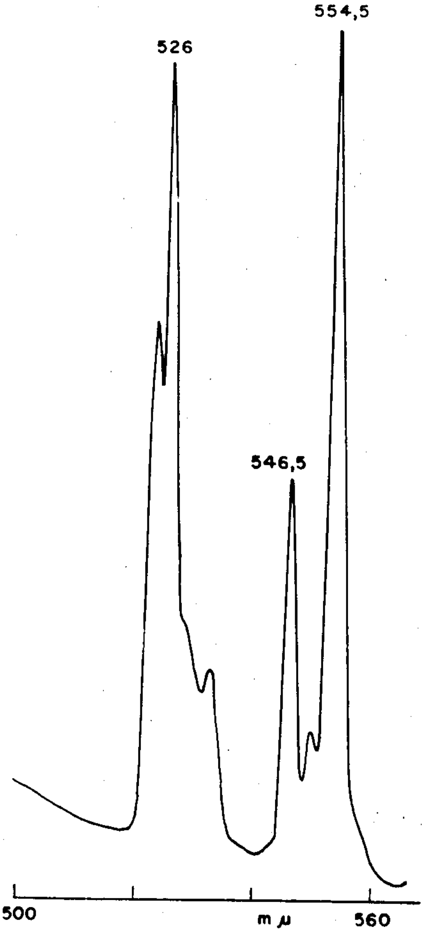

Fig. 14 - Emission spectrum of Er in YVO_4:
Er = 50 μg
Y = 100 mg
λe = 320 mμ

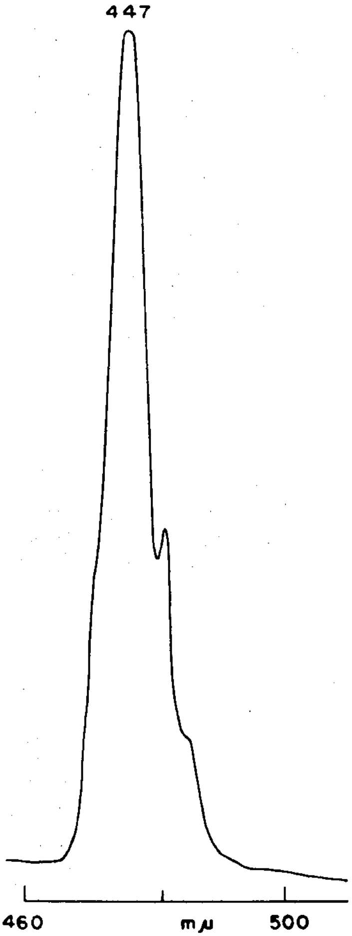

Fig. 15 - Emission spectrum of Tm in YVO_4.
Tm = 50 μg
Y = 100 mg
λe = 320 mμ

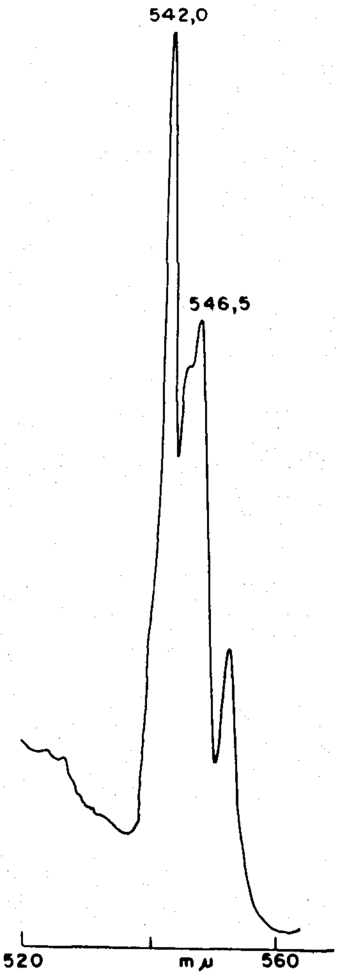

Fig. 16 - Emission spectrum of Ho in YVO_4.
Ho = 50 μg
Y = 100 mg
λe = 320 mμ

Figure 17 depicts the spectrum of all RE in a mixture (5 μg of each element) and 50 μg of thorium, in YVO_4 matrix.

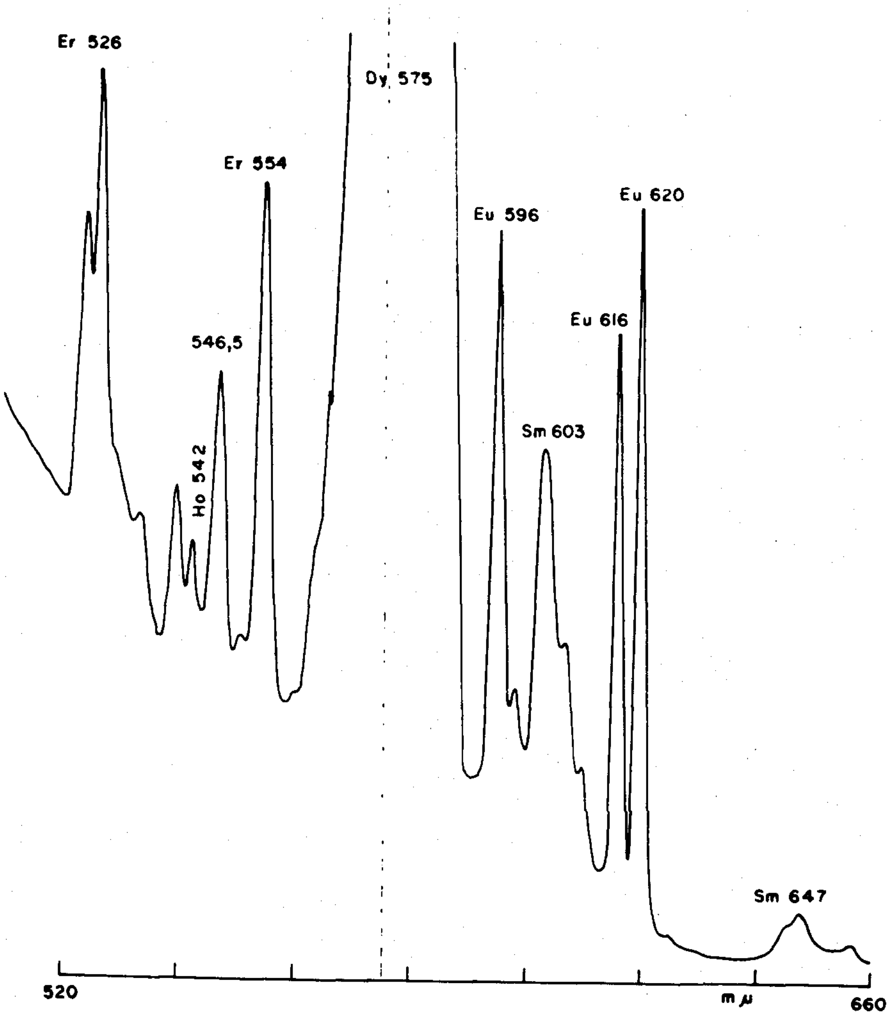

Fig. 17 - Emission spectrum of a mixed sample containing 5 μg of each rare earth and 50 μg of Th in an YVO_4 matrix.
λe = 320 mμ
Y = 100 mg

DETECTION LIMIT

Table III shows the detection limit for each RE in Y_2O_3 and YVO_4, respectively, the matrices prepared as described before and using 100 mg Y (127 mg Y_2O_3) for each sample.

TABLE III

RE fluorescence Detection Limit.
μg RE/100 mg Y.

El.	Y_2O_3	YVO_4	El.	Y_2O_3	YVO_4
La	n.f.	n.f.	Tb	0.01	n.f.
Ce	n.f.	n.f.	Dy	4	0.01
Pr	10	n.f.	Ho	4	2
Nd	IR	IR	Er	4	0.5
Sm	30	0.02	Tm	10	0.2
Eu	0.4	0.02	Yb	IR	IR
Gd	40	n.f.	Lu	n.f.	n.f.

n.f. = not fluorescent
IR = infrared

APPLICATION TO THE DETERMINATION OF RE IN NUCLEAR GRADE URANIUM

A series of experiments was performed using the proposed method for the separation, concentration and determination of RE in nuclear grade ammonium diuranate (ADU). Last traces of a 100 g U/l uranyl nitrate solution made 0.5 M in HF were removed by its percolation through a 2.0 ml Al_2O_3 column (fig. 1). To the effluent each one of tested RE was added and the uranyl nitrate solution percolated through a new Al_2O_3. The retained RE and Th were eluted with 50 ml hot 1.0 M HCl. The eluted solution was used for the RE determination. After comprovation of the excelence of the method, it was applied to the determination of RE in various samples of nuclear grade ADU. Table IV shows the results of some RE in one sample using the proposed method. 20 g of U were percolated through the column.

TABLE IV

RE content in ADU sample.
Results in μg RE/g U.

Ce	0.16
Eu	0.003
Dy	0.023
Sm	0.008
Ho	$<$ 0.2
Tb	0.08

In these ADU samples produced at the IEA Pilot Plant the other RE are much lower than the detection limit and as a consequence a much higher amount of uranium must be percolated through the column. Work for the determination of all possible RE by the spectrofluorimetric method here proposed is on progress.

CONCLUSION

For the determination of minor amounts of RE and Th present as impurities in nuclear grade uranium the separation and concentration by chromatography on Al_2O_3 the method described by Abrão/6/ has been widely and successfully used. The interference from uranium itself and from a number nonrare earths elements was eliminated by the present recommended procedure, through selective fixation of RE and Th on alumina and by precipitation of yttrium oxalate. In a general way the methods applied to the separation of RE from uranium have as consequence the presence of small amount of thorium, this element being very close to the RE and follows them in chemical procedures involving oxalate, fluoride, phosphate, and hydroxide precipitation.

In the present method, thorium, that accompanies the RE in uranium, is fixed on the alumina and eluted by hot HCl together with all RE and is copprecipitated with yttrium oxide used as solid matrix for RE spectrofluorimetric determination. As the procedure does not allow separation of thorium, the fluorimetric determination of RE was studied in its presence.

In this paper a modification of the chromatographic procedure was introduced and is concerning to the previous ignition of Al_2O_3 at 900°C. This previous treatment has a consequence the decrease of the capacity for RE retention but, on the other hand, it made the elution of RE and Th with hot 1,0 M HCl more easy and directly done in the column.

The use of yttrium was advantageous, acting as the matrix and standard and was preferred for this purpose because does not fluoresce.

The fluorescence exhibited nearly only by the lanthanides on solid Y_2O_3 and YVO_4 matrices permit the detection of 9 RE elements, some of them at a level as low as 0.01 μg/100 mg Y. Only six RE elements fluoresce in both matrices, the sensitivity in YVO_4 being always higher (see Table III).

Remarkable is the fact that while in Y_2O_3 each element exhibited a characteristic excitation, peaking at different values, in the YVO_4 matrix a rather broad band is observed, peaking at about 320 mμ. This implies that the YVO_4 matrix has a characteristic excitation fluorescence spectrum not influenced by other RE that contribute for the luminescent center formation. On the other hand, in the Y_2O_3 matrix the excitation fluorescent spectrum is peculiar to each one RE present, the excitation being more selective in this matrix.

Previous papers/32,33/ do not mention the fluorescence of Pr in Y_2O_3 at room temperature, only at low one. In the present work we observed the fluorescence of Pr in Y_2O_3 at room temperature, 10 μg of this element giving detectable fluorescence. Remarkable also is the fact that cerium, being highly fluorescent in inorganic acids and in thorium chloride or perchloride, does not fluoresce either in Y_2O_3 or in YVO_4.

Thorium does not fluoresce either in Y_2O_3 or in YVO_4 and then does not constitute interference even when present in amount 50 times greater than the RE. No difficulty was found by the collected thorium existing together with RE in the analysed ADU samples, since this product is proceeding from the industrial monazite processing.

Finally, the procedure here recommended opens the opportunity of determining extremely low amounts of RE in highly pure uranium compounds that are very difficult, if not impossible, to be determined by other techniques.

RESUMO

O trabalho descreve a determinação de microquantidades de terras raras em urânio por espectrofluorimetria. Os elementos das terras raras são separados e concentrados em uma pequena coluna de alumina (3 ml de Al_2O_3), após percolação de uma solução de nitrato de uranilo, em meio HF 0,3 M, em concentrações tão altas como 250 g U/litro.

O elemento tório, se presente, é também retido pela alumina. Os elementos das terras raras e tório são eluídos diretamente na coluna com HCl ou $HClO_4$ 1 M.

Os lantanídeos, após eluição, são determinados usando matriz sólida. Dy, Eu, Sm, Tm, Er e Ho são determinados em matriz de YVO_4, e Tb, Pr e Gd, em matriz de Y_2O_3. Embora os primeiros seis elementos citados apresentem fluorescência em Y_2O_3, suas intensidades de fluorescência são sensivelmente maiores em YVO_4.

O elemento cério, que não apresenta fluorescência, tanto em Y_2O_3 como YVO_4, é determinado diretamente no eluído. Ce-III é altamente fluorescente em ácidos inorgânicos diluídos e pode ser determinado, nestas soluções, em concentrações tão baixas como 0,001 μg/ml.

Nd e Yb também fluorescem em matriz sólida de Y_2O_3, mas suas bandas de fluorescência se encontram na região do infravermelho (800-1000 mμ) e não foram determinados neste trabalho. La e Lu não fluorescem em ambas as matrizes e também não foram determinados.

O procedimento tem sido aplicado para a determinação de terras raras em amostras contendo 20 gramas de urânio. Considerando-se esta massa de urânio, os limites inferiores de detecção alcançados, foram (μg de lantanídeo/g U): Dy-0,0005, Eu-0,001, Sm-0,001, Tm-0,0005, Er-0,02 e Ho-0,1, em matriz de YVO_4, e Tb-0,005, Pr-0,5 e Gd-2,0, em matriz de Y_2O_3; Ce-0,002, diretamente em solução de HCl ou $HClO_4$.

RÉSUMÉ

Ce travail décrit la détermination de microquantités de terres rares dans l'uranium par spectrofluorimetrie. Les éléments de terres rares sont séparés et concentrés dans une petite colonne d'alumine

3 ml de Al_2O_3) a partir d'une solution de nitrate d'uranile, dans un milieu HF 0,3 M, à des concentrations aussi élevées que 250 g U/litre.

L'élément thorium si prèsent est retenu par l'alumine. Les éléments de terres rares et le thorium sont élués directement dans la colonne avec HCl ou $HClO_4$, 1 M.

Les lantanides, aprés élution, sont déterminés en utilisant la matrice solide. Dy, Eu, Sm, Tm, Er et Ho sont déterminés à partir des matrices de YVO_4, et Tb, Pr et Gd à partir des matrices de Y_2O_3. Bien que les premiers six éléments soient fluorescents en présence de Y_2O_3, leurs intensités de fluorescence sont sensiblement plus grandes em présence de YVO_4.

L'élément cérium que ne présent pas de fluorescence, aussi bien en présence de Y_2O_3 qu'en présence de Y_2O_3 est déterminé directement dans l'élué. Ce-III, est trés fluorescent en présence d'ácides inorganiques et peut être déterminé dans ces solutions à des concentrations aussi basses que 0,001 μg/ml.

Nd et Yb également fluorescents dans une matrice solide de Y_2O_3 mais les bandes de fluorescences se trouvent dans la région infrarouge (800-1000 mμ) et n'ont pas été déterminés dans ce travail. La et Lu ne présentent pas de fluorescence dans aucune des 2 matrices et également n'ont pas été déterminés.

Là procédé a été appliqué pour la détermination de terres rares dans des échantillans contenant 20 grames d'uranium. Si l'on consideré cette masse d'uranium, les limites inférieurs attants, furent (μg de lantanide/g U): Dy-0,0005, Eu-0,001, Sm-0,001, Tm-0,0005, Er-0,02 et Ho-0,1, dans la matrice de YVO_4, et Tb-0,005, Pr-0,5 et Gd-2,0 dans une matrice de Y_2O_3, Ce-0,002 directement dans une solution de HCl ou $HClO_4$.

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