INVESTIGATIONS ON THE DETERMINATION OF YTTRIUM BY NEUTRON ACTIVATION ANALYSIS. APPLICATION OF THE SUBSTOICHIOMETRIC TECHNIQUE

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INVESTIGATIONS ON THE DETERMINATION OF YTTRIUM BY NEUTRON ACTIVATION ANALYSIS. APPLICATION OF THE SUBSTOICHIOMETRIC TECHNIQUE.*

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ABSTRACT

The separation of yttrium from lanthanide elements by extraction chromatography, using di(2-ethylhexyl) orthophosphoric acid (HDEHP) as the stationary phase, kieselguhr as the inert support and HNO_3 solution as the mobile phase, was studied.

More than 50% of yttrium, initially present, was obtained in the pure state, by eluting this element with a HNO_3 solution with concentration ranging from 4.5 N to 5.0 N.

The substoichiometric technique was applied to the determination of yttrium. This element was partially complexed with EDTA and the Y^{3+} ions remaining in the solution were separated from the (Y-EDTA) chelate by means of a cationic resin.

The sensitivity, precision and accuracy that may be expected in the analytical results were also studied.

INTRODUCTION

The knowledge of yttrium concentration in several materials, as for instance, minerals and alloys, presents interest. As far as minerals are concerned, the interest arises from both the economical aspect of mines explorations and the geological point of view in the investigation of the minerals origin, since, as pointed out by Morrison[2] "every element is of potential geochemical interest".

The investigation presented in this work arose from the demand of analyses of some toxic or cancerigenous elements, among them yttrium, present in flying ashes.

The analysis of yttrium is generally carried out by instrumental techniques, such as emission spectrometry, X-rays fluorescence, etc.

However, these techniques present limitations coming from the sample composition as well as from the yttrium concentration that is to be determined. Therefore, the development of new analytical techniques concerning this element is of interest not only as a contribution to its analytical chemistry, but also to confirm results of analyses obtained by instrumental methods.

The chemical behaviour of yttrium is very similar to that of the lanthanide elements. Neutrons activation analysis in one of the most sensitive methods used for the determination of almost all the lanthanides even when purely instrumental technique is applied. However, yttrium needs chemical separation, since, by neutron activation, it gives rise to ^{90}Y which is an essentially beta particles emissor. Since almost all the lanthanides are beta-particles emissors too, the separation of yttrium must, necessarily, be made from this group of elements.

The separation methods for lanthanides and yttrium as a group have already been carefully investigated[11] and they were also examined by radiochemical techniques[9]. Hence, in this paper, only the separation of yttrium from the lanthanide's group was investigated.

Taking into account the similarity of the chemical properties of these elements, it is easy to see the difficulty of obtaining their quantitative individual separation. Therefore, it is necessary to make use of a method that permits to calculate the chemical separation yields, so that results with good precision and accuracy may be got.

Yttrium and the lanthanides form very stable chelates with ethylenediaminetetraacetic acid (EDTA) and the stability of the yttrium chelate with EDTA is suitable for the application of the substoichiometric technique. This technique, that was introduced by Ruzicka and Stary[7] in activation analysis, avoids the determination of the chemical separation yield.

By adding a known amount of the complexing agent to an yttrium solution, it is possible to foresee the amount of the element that will be chelated, the excess of yttrium remaining as Y^{3+} ions. In this work, it was confirmed that at pH = 5.8 the chelate $(Y-EDTA)^-$ is formed and that it may be separated quantitatively from the Y^{3+} ions by using a cation exchanger.

The study of the best conditions for obtaining the separation of yttrium from the lanthanides was also undertaken. Extraction chromatography is the best separation technique for this purpose when little amounts of the elements are concerned, and one of the most suitable chelating agents to reach this aim is HDEHP. Sochacka and Siekirski[8], for instance, employed HDEHP for separating milligram amounts of erbium from microgram amounts of terbium. The extraction constant of the yttrium — HDEHP chelate has a value between those that were obtained for the holmium and erbium chelates formed with HDEHP, as stated by Qureshi et al.[6].

Erbium does not interfere with the determination of yttrium by neutron activation analysis, since ^{171}Er $(T_{1/2} \approx 7.8\ hours)$ formed is, comparatively to ^{90}Y $(T_{1/2} = 64.3\ hours)$, a short-lived radioisotope. Since the elution's sequence must be terbium, erbium, holmium, yttrium and tullium, it was tried, in this work, to repeat the procedure presented by Sochacka and Siekirski[8]. The separation efficiency was followed by means of radioactive tracers of the elements studied.

The first essay accomplished showed that it was quite impossible to obtain the expected separation. Therefore, the second purpose of this work was to look for the best conditions (column dimensions, elution flow rate and HNO_3 concentration) that would lead to a fraction of pure yttrium.

EXPERIMENTAL

Apparatus

1) Nuclear Chicago Model D-33, Geiger-Müller tube coupled to a Nuclear Chicago Model 8166 scaler.

2) Nuclear Chicago Model 8775, single-channel analyser coupled to a well-type 5.0 x 4.4 cm NaI(Tl) scintillation detector.

3) TMC Model 406-2, 400-channel analyser coupled to a well-type 7.5 x 7.5 cm NaI(Tl) scintillation detector.

REAGENTS AND SOLUTIONS

Amberlite resin CG — 120, type II, 200 mesh, in the R-NH$_4$ form.

Kieselguhr silanized, 0.2 — 0.3 mm, Merck.

Di(2-ethylhexyl) orthophosphoric acid, purified according to the procedure proposed by Peppard[5].

0.1 N NH$_4$OH solution.

HNO$_3$ solutions of several concentrations, pre-equilibrated with HDEHP.

Yttrium nitrate solution — 100 mg Y/ml.

Solutions of holmium, terbium and tullium nitrates — 2 mg of each element/ml.

Ferric chloride solution — 20 mg Fe/ml.

Ethylenediaminetetraacetic acid (EDTA) solutions: (A) 4,194 mg EDTA/ml; (B) 10 mg EDTA/ml, as the ammonium salt.

All the reagents were of analytical grade and deionized water was used throughout the chemical procedures.

Preparation of Radioactive Tracer Solutions

The radioactive tracers (^{90}Y, ^{160}Tb, ^{166}Ho and ^{170}Tm) were obtained by irradiation of the oxides of the respective elements, during a period of 8 hours in a thermal neutron flux of 5×10^{12} n cm^{-2} sec.$^{-1}$

The irradiated oxides were dissolved with HNO$_3$, the solutions were dried and the residues were taken with suitable volumes of deionized water.

PROCEDURE

I — Investigations on Substoichiometric Determinations of Yttrium

Fourteen solutions containing the same amount of yttrium (10 mg) and ^{90}Y tracer were prepared. These solutions were dried and then increasing volumes of solution A of EDTA were added, according to the following: two experiments were run with 2 ml of solution A, two experiments with 4 ml of solution A and so on, in such a way that the last experiments were carried out with 14 ml of solution A. Then 0,1 N NH$_4$OH solution was added in order to obtain pH = 5.8 and the volume was made up with water until a total volume of 15 ml. The solutions were then percolated through the columns (diameter = 5 mm; height = 60 mm) containing the cationic resin in the R-NH$_4$ form, at the flow-rate of 0.5 ml/min. The columns were washed with 10 ml of deionized water, and 1 ml of FeCl$_3$

solution was added to each effluent. Iron III displaces yttrium from the (Y-EDTA)⁻ chelate, since the stability constant of the (Fe – EDTA) chelate is about 10^7 times higher than that of the (Y-EDTA)⁻ chelate. A suitable amount of yttrium was added to each solution, in order to have the same amount of 20 mg in all of them. After adjusting the pH to about 2.5, yttrium oxalate was precipitated. The precipitates were filtered, dried and their activities were measured with the aid of a Geiger Müller counter. The recovered activities were compared to the activity of a standard prepared by precipitation, as oxalate, of 20 mg yttrium containing the same amount of ^{90}Y initially added to each experiment.

The results obtained are shown in Table I.

Table I

Substoichiometric Separation of Yttrium by Means of EDTA and
Cation Exchanger in the R-NH₄ Form

Experiment[*]	Mass of EDTA added (mg)	Y recovered (%)			
		Theoretical	Experimental		
			I	II	Mean
1	8.388	20	20.7	19.8	20.2
2	16.776	40	41.9	40.1	41.0
3	25.164	60	59.8	60.6	60.2
4	33.552	80	80.3	79.8	80.0
5	41.940	100	100.2	100.0	100.1
6	50.328	100	100.1	100.1	100.1
7	58.716	100	100.0	100.1	100.0

(*) The yttrium mass used in all experiments was of 10 mg.

Figure 1 presents the graphic obtained by plotting the mean values of each pair of parallel runs.
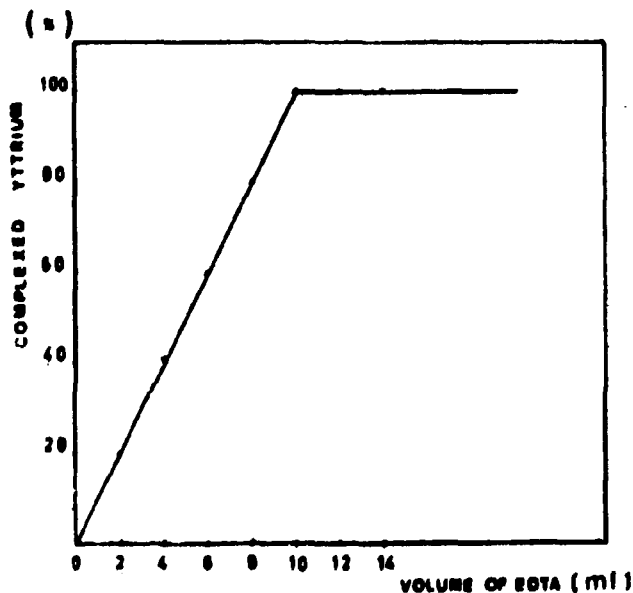

Figure 1 — Substoichiometric Complexation of Yttrium with EDTA

II — Separation of Yttrium from the Lanthanides by Extraction Chromatography

a) Preparation of the inert support — The silanized kieselguhr was grinded in an agate mortar and the fraction of grains between 0.074 and 0.105 mm was chosen as the support.

b) Preparation of the stationary phase — The HDEHP was dissolved in hexane keeping the proportion of 1 : 6 by volume. This solution was added to an amount of kieselguhr in such a way that the ratio between the mass of HDEHP and that of kieselguhr was 4 : 10. The mixture was stirred until almost all the hexane had evaporated and then the mixture was placed in a desiccator, remaining under vacuum for a period of, at least, two hours.

c) Preparation of the columns — The columns had 0.4 cm of diameter and 60 cm of height. Since the preparation of such a column is very difficult, use was made of the superposition of a 20 cm column above a column of 40 cm.
The impregnated kieselguhr was introduced into the column by means of a HNO_3 solution of the same concentration as that which would be used later for the elution.

d) Preparation of the Sample Solution

One ml of the yttrium, solution 0.5 ml of the other lanthanide solutions and known amounts of radioactive tracers of all of them, including ^{90}Y tracer were added to a little vial. After drying this solution, the residue was taken with 0.1 ml of HNO_3 of suitable concentration and it was introduced into the column. This operation was repeated twice more.

e) Elution — Regarding the elution, the best results were obtained when a solution of HNO_3 of concentration ranging from 4.5 to 5.0 N was used as eluant, and the flux was kept at $0.06 \, ml \, cm^{-2} \, min^{-1}$. The fractions were collected each 3 minutes (2 drops) and the total activity of each fraction was measured by means of a single-channel gamma-rays spectrometer. The activities of some fractions were measured also by means of the multi-channel analyser, in order to know their composition.

The elution curves obtained when 4.8N and 5.0N HNO_3 solutions were used as eluant are shown in Figures 2 and 3, respectively.

Estimation of the Method's Sensitivity

It was observed that, with the conditions adopted in this work (irradiation period = 8 hours, thermal neutron flux = $5 \times 10^{12} \, n \, cm^{-2} \, seg^{-1}$), the activity of ^{90}Y sample, placed at the nearest possible position from the Geiger tube, was 5500 cpm/mg of irradiated yttrium (as element). The time required for the analysis to be completed is of about 3 days, what means, approximately, one half-life of ^{90}Y (2.68 days).

The results shown in Figure 2 and Figure 3 enables one to admit that 20% of pure yttrium, at least, are recovered. If such is assumed, the initial ^{90}Y activity will be reduced to a tenth, namely, 550 cpm/mg of irradiated yttrium.

If the sample to be analysed contains 1 ppm of yttrium and a 200 mg sample is irradiated, the ^{90}Y activity will be 110 cpm.

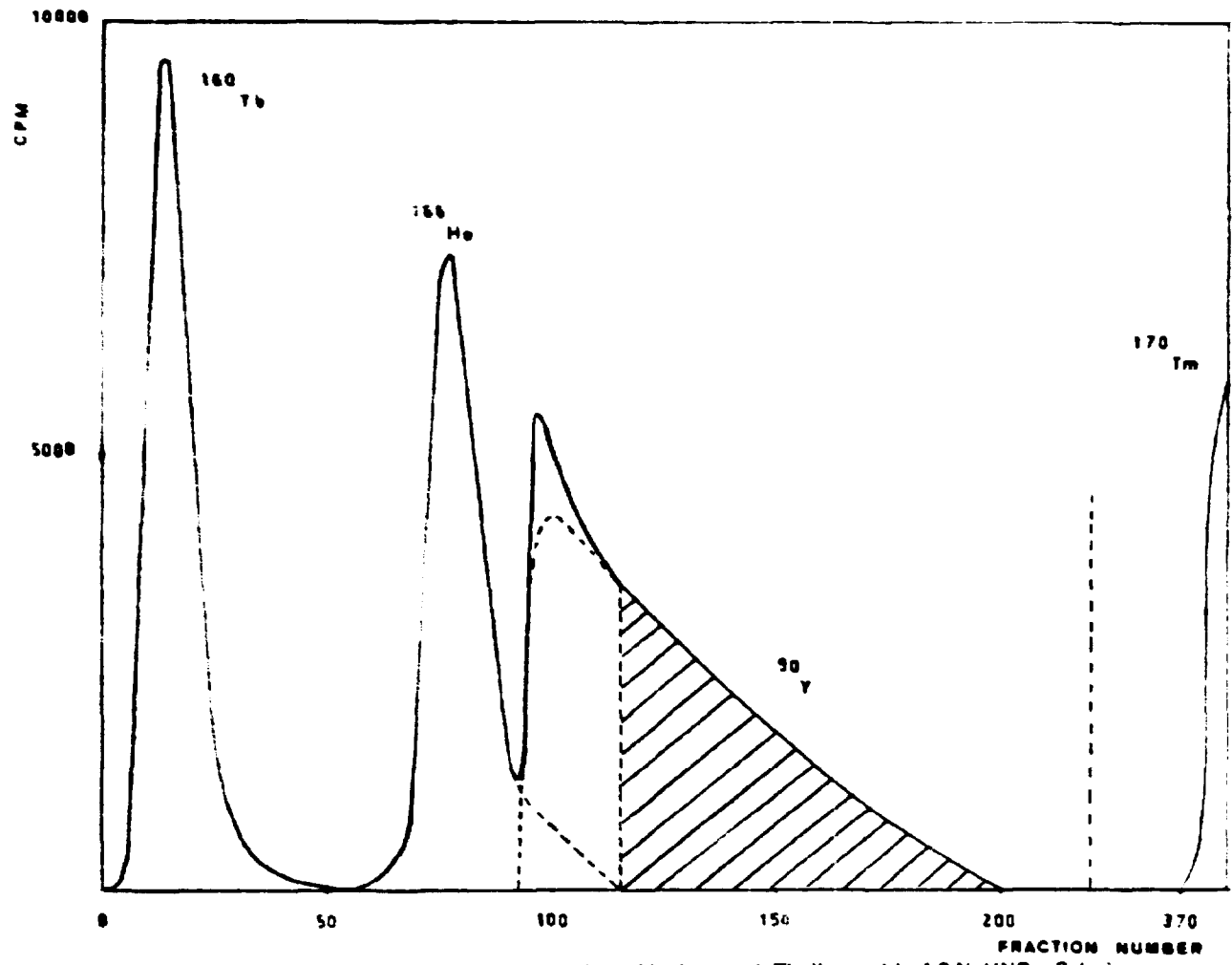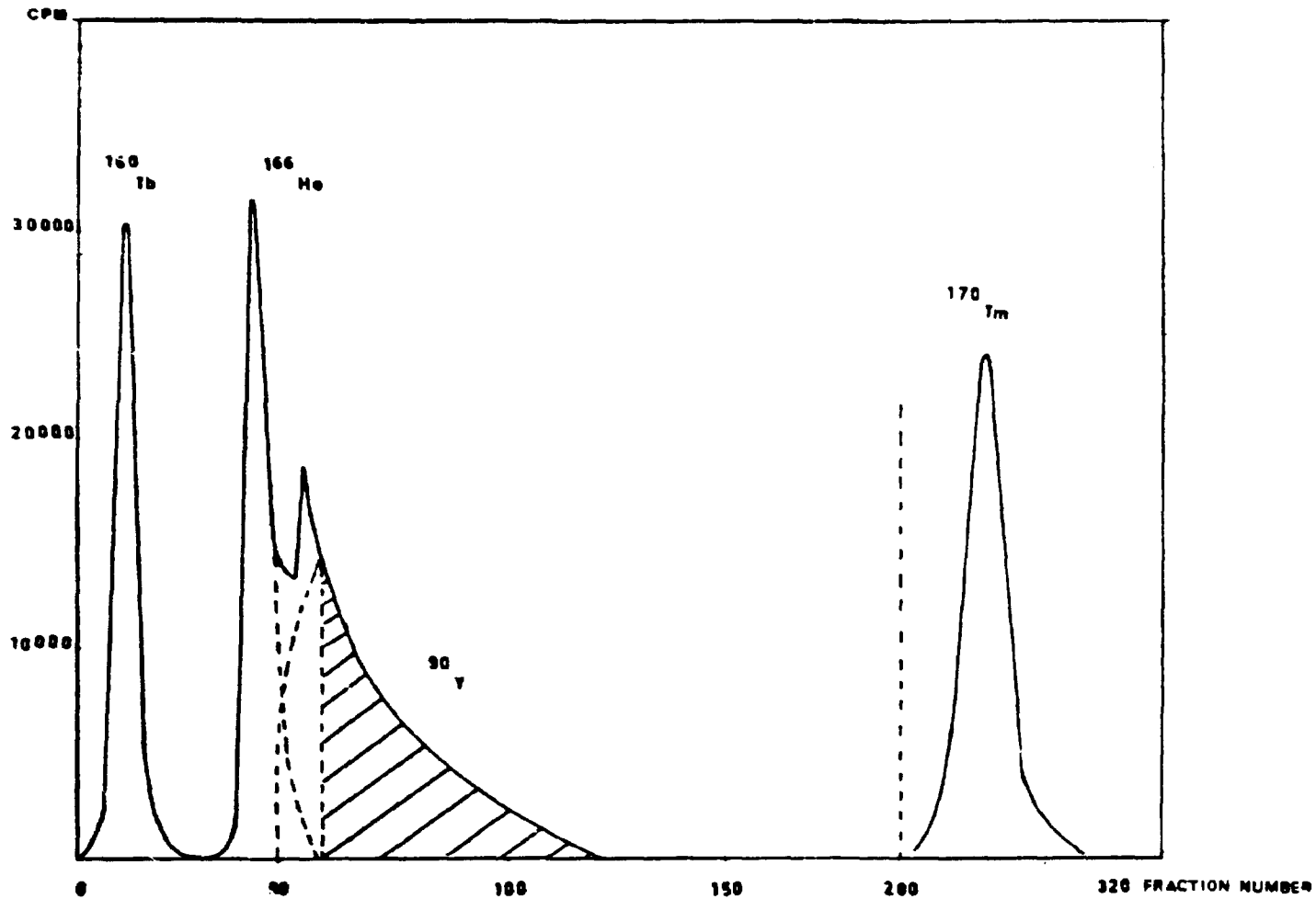Figure 2 — Elution Curves for Terbium, Holmium, Yttrium and Thulium with 4.8 N HNO₃ Solution

Figure 3 — Elution Curves for Terbium, Holmium, Yttrium and Thulium with 5.0 N HNO_3 Solution

By means of 100-minutes countings for the ^{90}Y of the sample as well as for the background (about 20 cpm), the result will be 110 ± 1.2 cpm.

According to Currie's criterion[1], a relative standard deviation of 10% in counting is allowable, when trace elements are analysed.

By keeping the irradiation and counting conditions as described above and by allowing for the errors already mentioned, it is possible to calculate the value of 7 cpm for the ^{90}Y activity which corresponds to 60 ppb of yttrium in the sample.

Accuracy of the Method

The five first results presented in Table I define a straight line. By applying the method of the least squares[3] to the theoretical values (x_i) and to the experimental results (y_i), the following equation of regression results for the straight line:

$$y = 0.695 + 0.994\, x \tag{I}$$

By applying the t-criterion[3] to the $a = 0.695$ and $b = 0.994$ parameters, it is possible to infer, with a confidence probability = 95% that $a = 0$ and $b = 1$. The values $a = 0$ and $b = 1$ show that the method studied is free from constant errors which would affect the accuracy of results.

Precision of the Method

According to the equation of regression (I), to the value $x^\circ = 20$ corresponds the value $y^\circ = 20.54$, where (x°, y°) is a point of the straight line. The imprecision of the correspondent experimental result may be estimated by means of a confidence interval which may be calculated by the following equation[10]:

$$y = y^\circ \pm ts \sqrt{1 + \frac{1}{n} + \frac{(x^\circ - \bar{x})^2}{\Sigma(x_i - \bar{x})^2}}$$

Where

      is the standard deviation of the regression

    $\bar{x}$ is the mean of the theoretical values x_i

    n is the number of determinations

In the case of $x^\circ = 20$, the experimental result is:

$$y = 20.54 \pm 1.71$$

It must be pointed out that the calculated imprecision of y does not include the counting errors, since the values presented in Table I were obtained by means of sufficiently high activities so that counting errors were negligible.

DISCUSSION

From the results presented in Figures 1 and 2, it can be seen that the extraction chromatography technique is efficient for the separation of milligram amounts of yttrium, However, the conditions applied in the chromatographic separation may, possibly, be improved if the following factors are considered: 1º) Grinding of the kieselguhr after it has been silanized may have damaged, at least partially, the properties acquired by means of the silanization process. So, the lanthanides and yttrium may have been absorbed by the support and the consequence of that in the elution would be the broadenning of the bands. 2º) The chelating agent (HDEHP) is not the best one for this purpose, since, according to Peppard et al.[4] (2-ethylhexyl) phenylphosphonic acid shows a better separation factor for adjacent rare earths.

Even though the conditions employed in this work have not been the best, the possibility of obtaining the separation of about 50% of the amount of yttrium, used in the experiments, was shown in Figure 1 and 2.

The substoichiometry applied to pure fractions of yttrium is not necessary in this work, since any other suitable method, for determination of yttrium would yield the same result. However, the possibility of fixing "a priori" the amount of yttrium to be recovered by the cation exchanger simplifies the analyses.

It is also possible, by applying the substoichiometric technique, to carry out parallel analyses in the same solution by making two successive separations of 20% of yttrium, since a separation yield for pure yttrium from the lanthanides of at least 50% has been obtained. Having this possibility in mind the sensitivity of the method was calculated for a substoichiometric separation of 20% of yttrium. It was shown that, with an irradiation period of 8 hours under a thermal neutron flux of 5×10^{12} n cm^{-2} sec^{-1}, it is possible to determine 60 ppb of yttrium in a 200 mg sample. The sensitivity may obviously be improved by using irradiation periods longer than 8 hours and also by using a higher flux of thermal neutrons. The sample mass might also be increased in order to have better sensitivity, but this is a problem which must be carefully examined, since the attenuation of the neutron flux in the sample by self-absorption may interfere with the accuracy of the results.

The investigation on the accuracy of the method, as fas as the substoichiometric determination of yttrium is concerned, allowed to conclude that there are no factors which may introduce systematic errors that would deviate the results values from the true ones.

It was also shown by Equation II that the precision may be expected if the irradiation and counting conditions are those used in this work, bears a relative standard deviation of about 8% at the 95% confidence probability.

Practical applications and the study of interferences that may be expected to arise from the fission of uranium and thorium, when these elements are present in the sample, have not been made until now. Therefore the investigation on the activation analysis of yttrium will be extended further and the purpose is to consider also the possibilities of the substoichiometric isotope dilution analysis, by using corrier free ^{90}Y as tracer.

RESUMO

Estudou-se a separação de ítrio dos elementos lantanídicos por cromatografia de extração, usando ácido di-(2-etilhexil) fosfórico (HDEHP) como fase estacionária, Keiselguhr silarizado como suporte inerte e solução de HNO₃ como fase móvel.

Mais do que 50% de ítrio, inicialmente presente, foi obtido no estado puro, pela eluição desse elemento com uma solução de HNO_3 numa faixa de concentração de 4,5 a 5,0 N.

A técnica substequiométrica foi aplicada à determinação de ítrio. Esse elemento foi parcialmente complexado com EDTA e os íons Y^{3+} que permaneceram na solução foram separados do quelato (Y-EDTA) por meio de uma resina catiônica.

Estudou-se a sensibilidade, precisão e exatidão que podem ser esperadas dos resultados analíticos.

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