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**SELECTIVE CONCENTRATION
OF THE LANTHANIDES
WITH SIMULTANEOUS PURIFICATION
FROM SCANDIUM**

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1. Introduction

For the determination of the rare earth elements (REE) in mineral samples by instrumental neutron activation analyses (INAA) it is necessary, as a rule, to undertake their preliminary chemical concentration and separation from the lightly activating impurities. Scandium, usually accompanying REE in mineral samples and in the process of the preliminary enrichment, is one of the admixtures which is most difficult to separate ^{/1/}. It is necessary to note that the relative content of REE and scandium in rocks is varied in wide limits: for example, in apatites it is 1:2.7·10⁵, but in ilmenites it is 100:1.7 ^{/2/}. The difficulties of REE determination in the scandium containing rocks by INAA become obvious, if we take into account that the average Scandium Clark in the earth core is higher than the REE Clark by a factor of 10-100 ^{/3/}.

The extraction-chromatography technique has certain advantages when mass analyses with the preliminary chemical enrichment are carried out. There are two techniques (solvent extraction ^{/4/} and extraction-chromatography ^{/5/}) described in the literature which are applicable for scandium-lanthanide separation. They are based on systems with hydrochloric acid-triethylphosphine oxide (TOPO) as an extractant. However, both of them have low selectivity with respect to the lanthanides and require a number of additional operations.

In the present work a new technique for the selective extraction-chromatographic concentration of the REE with simultaneous separation from scandium and practically from all the other accompanying elements is suggested. TOPO is used as a fixed phase here. The extraction of the REE and scandium is carried out at the sorption stage from solutions containing a strong complexing agent (diethylenetriamine-pentanoic acid (DTPA)), lactic acid and a salting-out agent. Then the selective elution of the REE is accomplished by 7 mol/l hydrochloric acid. This technique was previously developed for selective recovery of the rare earth and transplutonium isotopes from cyclotron target material after its irradiation by heavy ions accelerated at the cyclotron of the Laboratory of Nuclear Reactions of the JINR, Dubna ^{/6/}.

The application of methods of many elements (apart from Al, as was the case in work ^{/11/}), such as Cu, Co, Ni, Zn, Cd, Pb, Fe, is considered in the present study. It is especially important in the analysis of many mineral samples containing Cu, Zn, Fe and other

elements as macrocomponents which can automatically serve as salting-out agents for the REE and scandium extraction, essentially simplifying the whole procedure of the analysis.

2. Experimental

The solvent extraction behaviour of the REE, yttrium and scandium was systematically studied in systems with various aqueous solutions under different conditions. The 0.1-0.4 mol/l solutions of TOPO in benzene were applied as extractants. Trace amounts of ^{44}Sc , ^{88}Y , ^{140}La , ^{139}Ce , ^{143}Pm , ^{153}Sm , ^{152}Eu , ^{146}Gd , ^{160}Tb , ^{170}Tm , ^{173}Lu have been used in this work.

In the extraction experiments we used the following procedure. A 0.07 mol/l solution of DTPA in 1 mol/l lactic acid containing some quantity of HNO_3 necessary for supporting definite acidity was added to the nitrate (or hydroxide) of the element studied labelled by the corresponding radioactive tracer and containing a salting-out agent. After the complete dissolution of all components an equal volume of the extractant was added and the mixture was shaken for 15 minutes at room temperature. A preliminary experiment has shown that the equilibrium is achieved after about 5 min. Aliquots were taken from both organic and aqueous phases and the γ -activity of the samples was measured at the same geometry.

Glass columns with a diameter of 3 mm and a height of 60-80 mm were used in extraction-chromatographic experiments. Wofatit EP-60 (non-ionic macroporous copolymer of styrene and divinylbenzene) used as supporting agent was mixed with the corresponding amount of TOPO solution in benzene, which was then evaporated. The weight ratio of the extractant (TOPO) to the supporting material was 1:4.

3. Results

For the selection of optimal conditions for the REE and scandium separation the extraction and back extraction of both REE and scandium have been studied, depending on aqueous phase acidity, the extractant concentration, the type and concentration of the salting-out agents.

The results of the extraction of some REE (from La to Lu), yttrium and scandium by TOPO from DTPA solution in lactic acid containing $\text{Cu}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ as salting-out agents are presented in Fig. 1. An effect was observed in the other systems with phosphoric oxide extractants, a dome shaped dependency of K_d upon the atomic number of the element with a maximum at Sm, is a characteristic of

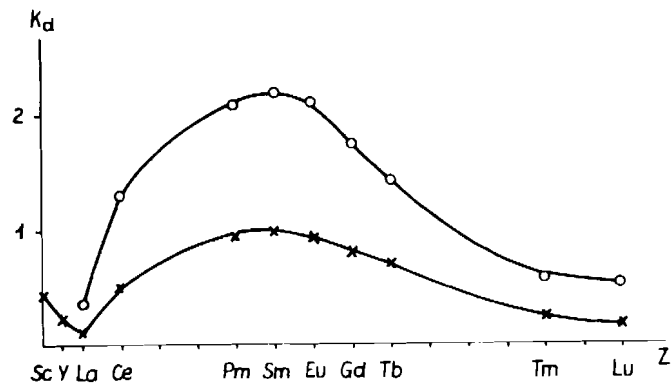


Fig. 1. Distribution ratios for REE, Y and Sc. Aqueous phase: 0.07 M DTPA, 1 M lactic acid (o) 0.5 M $\text{Al}(\text{NO}_3)_3$ (x) 0.5 M $\text{Cu}(\text{NO}_3)_2$ organic phase: 0.1 M TOPO in benzene.

the system. The yttrium and scandium behaviour in this case corresponds to the behaviour of the lightest and the heaviest REE. The plot of $\lg K_d$ versus \lg TOPO for the REE, yttrium and scandium has the form of a straight line with an angle coefficient equal to 3 (Fig. 2), demonstrating the same extraction mechanism for all these elements, resulting in formation of tri-nitrate of the composition, $\text{M}(\text{NO}_3)_3 \cdot 3\text{TOPO}$. The thulium and scandium isotherms (Fig. 3) show that for Tm K_d is practically constant up to a concentration of 10^{-1} mol/l and K_d for Sc remain unchanged up to 2×10^{-2} mol/l.

The influence of the salting-out agent concentration on the extraction of the REE and scandium from the DTPA-lactic acid solution was studied separately. As can be seen from the data of Fig. 4, there is no difference between scandium extraction and that of the REE till the $\text{Cu}(\text{NO}_3)_2$ concentration reaches the value 1.0 mol/l. Above that concentration the scandium distribution coefficients continue to grow while the K_d values of all the REE begin to decrease, being by a factor of 10 lower than K_d of scandium when the concentration of the salting-out agent reaches 2.4 mol/l. This effect is probably due to the fact that the extraction efficiency of the REE and yttrium is much more sensitive to the solution acidity pH .

In fact, the influence of acid concentration on the REE and yttrium extraction by TOPO and on the extraction of scandium is quite different (Fig. 5). With increasing HCl concentration the Sc

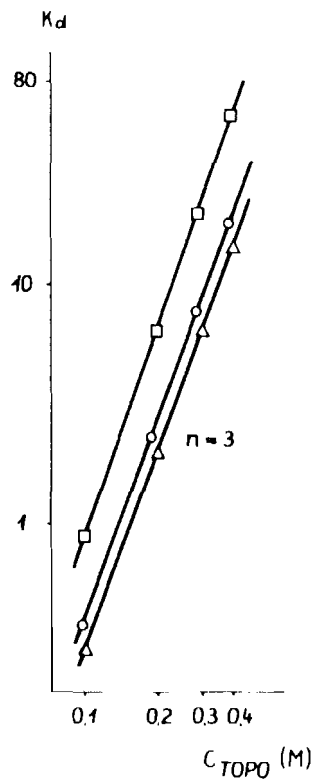


Fig. 2. Distribution ratios for Tm (Δ), Y (\circ) and Sc (\square) as functions of the analytical concentration of the extractant.

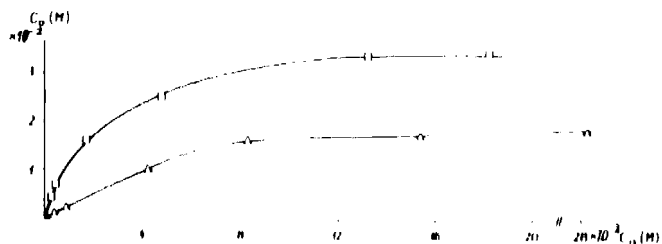


Fig. 3. The equilibrium organic phase concentration of Tm (Δ) and Sc (\square) as a function of their equilibrium aqueous phase concentration. Organic phase: 0.1 M TOPO in benzene.

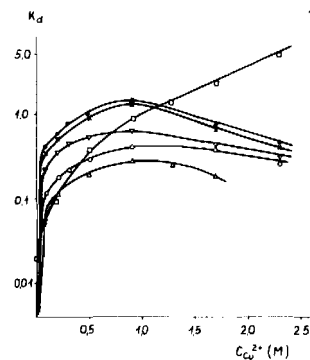


Fig. 4. The effect of salting-out agent concentration on the distribution ratios of Tm (Δ), Ce (∇), Eu (\times), Pm (\bullet), Y (\circ). Organic phase: 0.1 M TOPO in benzene.

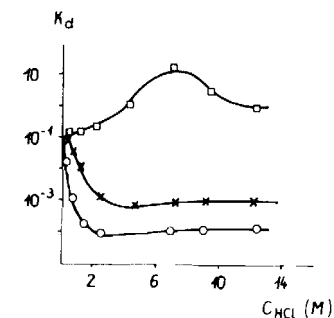


Fig. 5. Distribution ratios of Sc (\square), Y (\circ) and Tb (\times) as functions of the concentration of HCl. Organic phase: 0.1 M TOPO in benzene.

extraction goes through the maximum at about 7 mol/l ($K_d=17$) remaining rather efficient in the whole HCl concentration interval, while the extraction of the REE and yttrium sharply decreases (K_d falls down to 10^{-4} for Y and to 10^{-3} for the REE) beginning from 1 mol/l HCl concentration. This difference allows one to reextract the REE completely, leaving scandium in the organic phase.

The application of all the regularities observed allows one to develop and realize the extraction-chromatographic technique for the recovery of the REE and yttrium and for their separation from scandium and practically all the other elements present in micro- and macroconcentrations.

A number of the most abundant macrocomponents has been studied in this work with a view of using them as salting-out agents, because many of them can be present in naturally occurring and man-made materials. The results obtained (see the Table) show that all the salt considered can serve as salting-out agents with similar efficiency in the extraction system of DTPA in hydrochloric acid - TOPO. Relatively low distribution coefficients should not mislead the reader since they correspond to 0.1 mol/l concentration of TOPO, while practically 100% extractant is used in the extraction-chromatographic column (see Fig. 2). The column capacity is determined by the quantity of the extractant in the column.

Table

The effect of salting-out agent on the extraction of REE, yttrium and scandium by TOPO

Salting-out agent		$[H^+]$ (mol/l)	K_d				
Salt	Concentration (mol/l)		Ce	Tb	Tm	Y	Sc
$Al(NO_3)_3$	0.45	0.35	1.31	1.45	0.57	1.04	0.76
$Fe(NO_3)_3$	0.50	0.30	0.77	1.01	0.40	0.43	0.51
$Cu(NO_3)_2$	0.48	0.30	0.50	0.67	0.26	0.30	0.44
$Co(NO_3)_2$	0.50	0.28	0.48	0.64	0.18	0.24	0.37
$Ni(NO_3)_2$	0.48	0.20	0.45	0.60	0.15	0.23	0.35
$Zn(NO_3)_2$	0.50	0.36	0.50	0.87	0.22	0.24	0.34
$Ca(NO_3)_2$	0.50	0.03	0.46	0.31	0.10		0.15
$Gd(NO_3)_2$	0.50	0.24	0.44	0.46	0.19	0.16	
$Pb(NO_3)_2$	0.48	0.17	0.34	0.30	0.10		0.15
-	-	0.01	0.003	0.005	0.001	0.002	0.02

Then the quantitative recovery of the REE and scandium from nitrate solutions is achieved at the sorption stage. The solution containing not less than 0.5 mol/l of aluminium nitrate or another salting-out agent, 0.07 mol/l of DTPA and 1.0 mol/l of lactic acid is pumped through the column at a rate of not more than 1.5 ml/cm² min. Then the column is washed by a 3 mol/l solution of NH_4NO_3 and then by water. After pumping through the column the washing solution contains the complexing agent, the salting-out agent and all the other salt contaminants. After the washing stage to complete the REE are stripped by 7 mol/l HCl and then scandium by diluted HCl (≤ 1 mol/l) or by water. An example of such an extraction chromatographic REE recovery involving scandium separation is represented in Fig. 6. The γ spectrometric analysis of the REE fraction show no detectable amount of scandium.

The technique described allows one to achieve the efficient and easy separation of the REE and yttrium from scandium and many other accompanying substances.

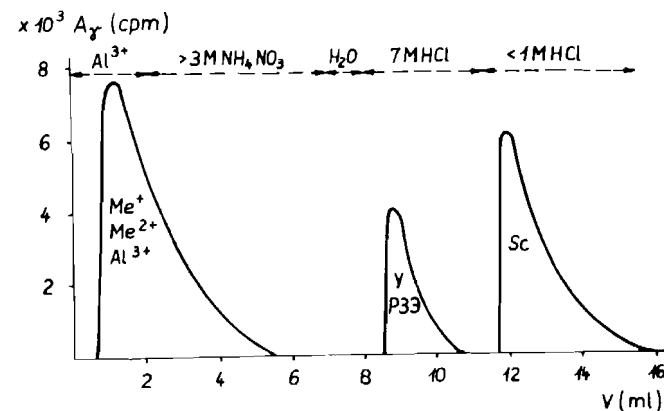


Fig. 6. Elution curves of group separation of REE and Y from macrocomponents and Sc.

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