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Studies on separation of rare earth elements on various types of anion-exchangers in the $C_3H_7OH-7 M HNO_3$ systems

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Abstract

This paper presents the possibilities of separation of yttrium(III)–neodymium(III) and samarium(III)–neodymium(III) pairs by frontal analysis on strongly basic anion-exchangers Wofatit SBW, Wofatit SBK and Lewatit MP 5080 in the systems: 90% (v/v) 2-propanol–10% (v/v) 7 M HNO_3 and 90% (v/v) 1-propanol–10% (v/v) 7 M HNO_3 . The best results are obtained on Lewatit MP 5080 in the 90% (v/v) 2-propanol–10% (v/v) 7 M HNO_3 system. In this system, on 1 dm³ of this anion-exchanger, 1.95 kg yttrium(III) and 0.3 kg samarium(III) were purified decreasing the microcomponent content to below 10⁻³%. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Anion-exchangers; Mobile phase composition; Rare earth elements; 1-Propanol; 2-Propanol

1. Introduction

Contrary to their name, rare earth elements are not rare at all. They are found in 200 minerals and the earth crust contains more of them, for example nickel, copper, tin and lead. The atmosphere, water, and soil as well as plants and animals [1–3] make a huge, complex system of circulating elements. This cycle also includes rare earth elements. This dynamic process covers atmospheric and geological phenomena as well as hydrological cycles and intensive human activity. A main source of rare earth elements are their own minerals or minerals of other elements accompanied by lanthanides. A secondary source can be industrial wastes formed as a by-product of some technologies. Of all mineral raw materials exploited

at present, the rare earth elements are most important for promoting modern technology. High purity yttrium is applied, among others, for production of lasers, luminophores [4,5], and magnetic superconductive materials [6–9], and for stabilization of ceramic material structures [10,11], catalysts [12], etc.

As rare earth elements occur together, their physico-chemical properties are similar and their separation is a difficult and expensive process. One of the methods allowing for rare earth elements separation is ion-exchange chromatography. From a practical point of view, a disadvantage of ion-exchange separation is the application of polystyrenesulphonate cation-exchangers of slightly differentiated ion-exchange affinity in relation to individual rare earth elements. So far there has not been a perfect eluent which would enable both selective separation of light, medium, and heavy

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lanthanides and yttrium removal, and would secure their high concentrations in the eluate. Therefore studies on the development of a simple and economic method of rare earth element separation are being carried out in numerous scientific centres around the world. Interesting results were obtained by using solid or liquid anion-exchangers for the separation of complexes of rare earth elements(III) with organic and inorganic ligands. The literature includes much data about the separation of micro- or milligram amounts of rare earth elements on anion-exchangers. Solutions of nitric acid, lithium, aluminium, magnesium, calcium and ammonium nitrates in aqueous–organic solvents were used as the eluants [13,14]. Recently it has been demonstrated that sodium trimetaphosphate is a very suitable new elution agent for the separation of rare earths and thorium on strongly basic anion-exchange resins [15,16].

Much attention has been given to the separation of rare earth elements(III) present in nitrate solutions on anion-exchangers. Rare earth elements(III) with NO_3^- in the aqueous solution form poorly stable, positive, neutral or negative complexes of the composition $\text{Ln}(\text{NO}_3)_n^{3-n}$ where n can assume values from 1 to 6.

Analysis of the literature data suggests that the most common cation complexes of $\text{Ln}(\text{NO}_3)^{2+}$ are the most stable in the middle position of lanthanide series [17–19]. The sizes of stability constants given by various authors are not comparable in some cases. Depending on the measurement technique, the sizes of different orders are obtained. No practical conclusions can be drawn about stability of the anion complexes $\text{Ln}(\text{NO}_3)_n^{3-n}$ except for the fact that it decreases as the atomic number increases or the complexing ion charge decreases. The differences in the values of distribution coefficients of nitrate complexes of rare earth elements(III) even in concentrated solutions of nitric acid are too small for their effective separation on anion-exchangers [19–21]. Moreover, concentrated nitric acid is strongly destructive for anion-exchangers [22] which makes it impossible to use this system in the macro-scale. In practice anion-exchangers were used only for separation of thorium(IV) and uranium(IV, VI) from rare earth elements(III) from mineral acid solutions. The limited possibilities of sorption and separation of rare earth elements(III) from aqueous solutions of nitric

acid are improved significantly in systems with a polar organic solvent.

Reports in the literature concerning this problem are often controversial. The papers by Korkisch and Marcus [13,14] provided many data enabling determination of optimal conditions of sorption of microquantities of rare earth elements(III) on strongly basic anion-exchangers: as follows from these studies the addition of organic solvent facilitates this process. However, this effect is the same for all ions of rare earth elements(III). Therefore their mutual separation does not improve. Moreover, a similar increase in the values of the distribution coefficients is obtained for many other elements which indicates that organic solvents may not improve separation of rare earth elements(III) from the elements of other groups.

Previous studies of sorption and separation of rare earth elements(III) in the polar organic solvent– H_2O – HNO_3 system indicate the possibility of ion-exchange separation of rare earth elements(III) in the macro–micro component system. The detection of changes in the affinity series of complexing ions of rare earth elements(III) for the anion-exchanger is of great importance depending on the mobile phase composition. The observed differences in the affinity series of complexing ions of $\text{Ln}(\text{NO}_3)_n^{3-n}$ type may be caused by changes of stability, charge (e.g. $\text{Nd}(\text{NO}_3)_5^{2-}$ and $\text{Y}(\text{NO}_3)_4^-$), structure and also solvation of these complexes. Different affinity series and also atypical behaviour of yttrium(III) compared with lanthanides(III) provide the possibility for separation and preparation of very pure substances which is of great significance in hydrometallurgy [23–26].

The aim of this paper is to study the effect of cross-linking effect of the strongly basic anion-exchanger Wofatit SBW on the effectiveness of separation of Y(III)–Nd(III) and Sm(III)–Nd(III) pairs by frontal analysis in the systems: 90% (v/v) 1-propanol–10% (v/v) 7 M HNO_3 and 90% (v/v) 2-propanol–10% (v/v) 7 M HNO_3 .

2. Experimental

2.1. Chemicals

All chemicals were of suprapur grade from POCH

Lublin, Poland. Yttrium(III), neodymium(III) and samarium(III) oxides of 99.9% purity were supplied by Fluka, Switzerland. The anion-exchangers were used in the nitrate form.

2.2. Equipment

The separation by frontal analysis was carried out in glass columns of 2-cm diameter. The percentage of neodymium in yttrium and samarium was determined by means of spectrophotometric analysis using a spectrophotometer Specord M 40 supplied by Zeiss, Germany.

2.3. Procedure

Separation of nitrate complexes of yttrium(III) from neodymium(III) and samarium(III) from neodymium(III) (~1%) on Wofatit SBW of various cross-linkings or Lewatit MP 5080 and Wofatit SBK×7% divinylbenzene (DVB) in 2-propanol or 1-propanol–H₂O–7 M HNO₃ systems was investigated. The anion-exchangers in the nitrate form were placed in the beaker with the corresponding solutions of HNO₃–polar organic solvent for ~24 h. The separation by frontal analysis was carried out in glass columns of 2-cm diameter filled with the anion-exchanger (50 cm³) at 22 °C. The solution of rare earth elements was prepared by dissolving the oxide in stoichiometric quantity of HNO₃ (1–2% excess) while heating. The nitrates of rare earth elements were next dissolved in the mixtures: 90% (v/v) 2-propanol–10% (v/v) 7 M HNO₃, and 90% (v/v)

1-propanol–10% (v/v) 7 M HNO₃. Rare earth element nitrate solutions of concentration ~25.00 g Ln₂O₃/dm³ (Y(III)–Nd(III)) and 5.23 g Ln₂O₃/dm³ (Sm(III)–Nd(III)) in the above mentioned systems were passed through the columns continuously at a flow rate of ~0.2 cm³/cm²×min. The effluent was collected in fractions of ~100 cm³ from which oxalates were precipitated and converted to oxides.

Determinations of neodymium(III) were made by means of a direct method using the neodymium absorption maximum for λ=794.3 nm. The solutions of rare earth element chlorides were found to have a concentration of ~0.5 g Ln₂O₃ in 10 cm³ of 2 M hydrochloric acid solution. The detection limit of neodymium(III) in samarium(III) under these conditions was 0.001%.

The results of purification of yttrium(III) from neodymium(III) and samarium(III) from neodymium(III) in the aqueous-polar organic solvent medium of nitric acid are presented in Tables 1–2. The concentrations of neodymium as a micro component in the effluent are shown graphically in Figs. 1–4.

The curves make it possible to calculate the weight K_d distribution coefficients for the micro component ion [27]:

$$K_d = \frac{(\bar{U} - U_0 - V)}{m_j}$$

The bed K'_d distribution coefficient is:

$$K'_d = K_d \cdot d_z$$

Table 1

The results of purification of yttrium(III) from 1% neodymium(III) (concentration: 25.00 g Ln₂O₃/dm³) in the 90% (v/v) 2-propanol or 1-propanol–10% (v/v) 7 M HNO₃ system on various types of anion-exchangers

Anion-exchanger	2-Propanol				1-Propanol			
	<i>m</i>	K_d	K'_d	<i>N</i>	<i>m</i>	K_d	K'_d	<i>N</i>
Wofatit SBW×2% DVB	–	92.25	15.48	1	2.21	71.39	11.98	9
Wofatit SBW×4% DVB	2.37	27.95	14.48	2	22.97	66.56	34.48	9
Wofatit SBW×6% DVB	52.83	199.94	65.98	14	44.73	162.06	53.48	19
Wofatit SBW×8% DVB	24.50	87.13	45.48	5	41.78	90.96	47.48	40
Wofatit SBW×12% DVB	–	29.32	10.48	1	6.45	60.10	21.48	3
Wofatit SBW×16% DVB	–	14.92	9.48	1	–	10.21	6.48	1
Wofatit SBK×7% DVB	10.27	88.94	47.88	3	10.80	75.56	40.68	6
Lewatit MP 5080	97.66	275.31	88.98	1953	75.73	214.98	69.48	753

m, amount of Y₂O₃<10⁻³% Nd₂O₃ purified on 50 cm³ of anion-exchangers (g).

Table 2

The results of purification of samarium(III) from 1% neodymium(III) (concentration: 5.231 g $\text{Ln}_2\text{O}_3/\text{dm}^3$) in the 90% (v/v) 2-propanol or 1-propanol–10% (v/v) 7 M HNO_3 system on various types of anion-exchangers

Anion-exchanger	2-Propanol				1-Propanol			
	m	K_d	K'_d	N	m	K_d	K'_d	N
Wofatit SBW×4% DVB	–	24.86	12.88	4	–	27.95	14.48	8
Wofatit SBW×6% DVB	–	61.45	20.28	11	–	102.97	33.98	3
Wofatit SBW×8% DVB	–	49.58	25.88	16	0.95	64.14	33.48	12
Wofatit SBW×12% DVB	–	31.00	11.08	120	–	34.92	12.48	3
Wofatit SBK×7% DVB	–	38.04	20.48	1	0.61	57.55	30.98	5
Lewatit MP 5080	14.76	270.67	87.48	97	10.46	211.88	68.48	87

m , amount of $\text{Y}_2\text{O}_3 < 10^{-3}\%$ Nd_2O_3 purified on 50 cm^3 of anion-exchangers (g).

The number of theoretical plates N can be calculated from:

$$N = \frac{(\bar{U} - U_0)(U' - U_0)}{(\bar{U} - U')^2}$$

where: K_d is the weight distribution coefficient, K'_d is the bed distribution coefficient, N is the number of

theoretical plates, \bar{U} is the effluent volume (cm^3) at $c = c_0/2$ (determined graphically), U_0 is the dead volume (cm^3) in the column (6 cm^3), V is the void (inter particle) resin bed volume (cm^3) which amounts to ~ 0.4 of the resin bed volume, m_j is the dry resin weight (g), d_z is the bed density (Table 3), and U' is the effluent volume at $c = 0.159 c_0$ (determined graphically).

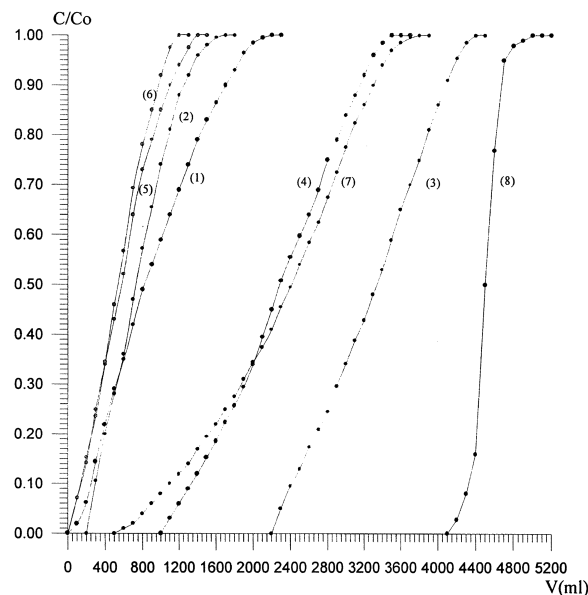


Fig. 1. The break-through curves for neodymium(III) in 90% (v/v) 2-propanol–10% (v/v) 7 M HNO_3 system on Wofatit SBW (SBK and Lewatit MP 5080) on various cross-linkings: (1) Wofatit SBW×2% DVB, (2) Wofatit SBW×4% DVB, (3) Wofatit SBW×6% DVB, (4) Wofatit SBW×8% DVB, (5) Wofatit SBW×12% DVB, (6) Wofatit SBW×16% DVB, (7) Wofatit SBK×7% DVB, (8) Lewatit MP 5080.

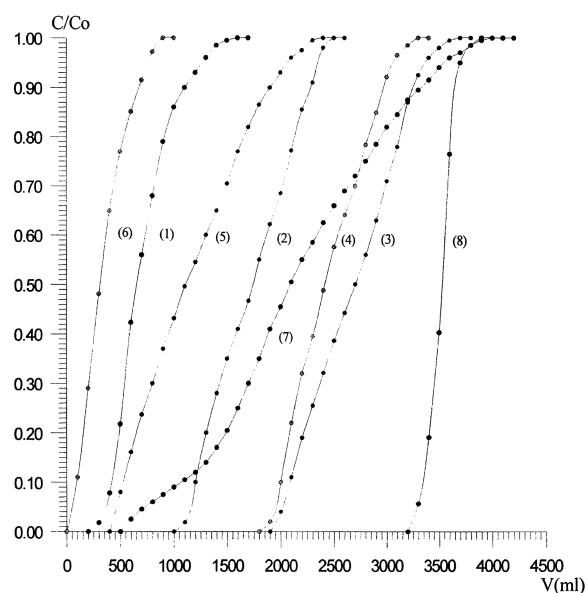


Fig. 2. The break-through curves for neodymium(III) in 90% (v/v) 1-propanol–10% (v/v) 7 M HNO_3 system on Wofatit SBW (SBK and Lewatit MP 5080) on various cross-linkings: (1) Wofatit SBW×2% DVB, (2) Wofatit SBW×4% DVB, (3) Wofatit SBW×6% DVB, (4) Wofatit SBW×8% DVB, (5) Wofatit SBW×12% DVB, (6) Wofatit SBW×16% DVB, (7) Wofatit SBK×7% DVB, (8) Lewatit MP 5080.

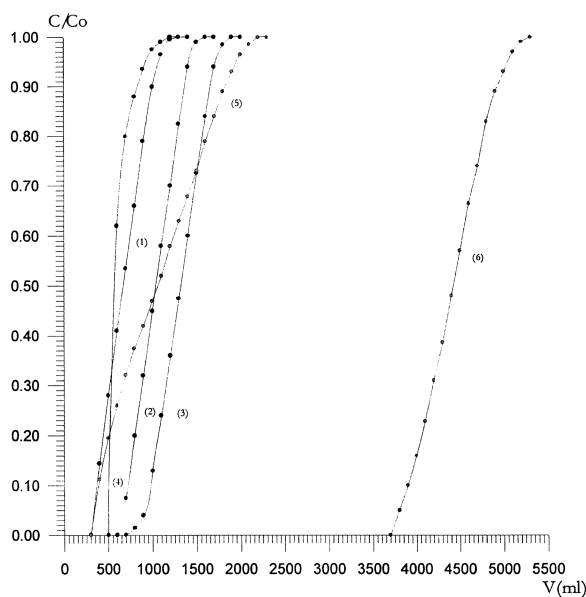


Fig. 3. The break-through curves for neodymium(III) in 90% (v/v) 2-propanol–10% (v/v) 7 M HNO₃ system on Wofatit SBW (Lewatit MP 5080) on various cross-linkings: (1) Wofatit SBW × 4% DVB, (2) Wofatit SBW × 6% DVB, (3) Wofatit SBW × 8% DVB, (4) Wofatit SBW × 12% DVB, (5) Wofatit SBK × 7% DVB, (6) Lewatit MP 5080.

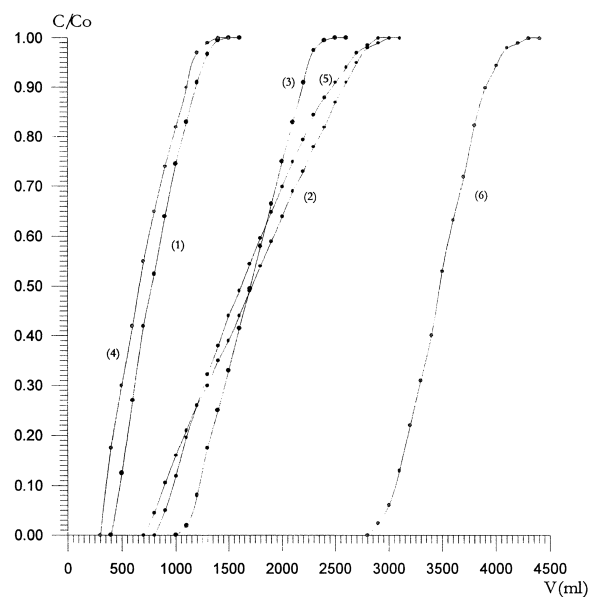


Fig. 4. The break-through curves for neodymium(III) in 90% (v/v) 1-propanol–10% (v/v) 7 M HNO₃ system on Wofatit SBW (Lewatit MP 5080) on various cross-linkings: (1) Wofatit SBW × 4% DVB, (2) Wofatit SBW × 6% DVB, (3) Wofatit SBW × 8% DVB, (4) Wofatit SBW × 12% DVB, (5) Wofatit SBK × 7% DVB, (6) Lewatit MP 5080.

3. Results and discussion

In the separation process of both yttrium(III)–neodymium(III) and samarium(III)–neodymium(III) pairs, the best results were obtained, as studied by us previously, in the systems with other organic solvents (methanol, ethanol, acetone) [23–26] on the strongly basic macroporous anion-exchanger Lewatit MP 5080. In the system 90% (v/v) 2-propanol–10% (v/v) 7 M HNO₃ ~2.0 kg of yttrium(III) and 0.3 kg of samarium(III) can be purified on 1-dm³ bed in the nitrate form and in the system 90% (v/v) 1-propanol–10% (v/v) 7 M HNO₃ 1.5 kg of yttrium(III) and 0.2 kg of samarium(III) decreasing the microcomponent content to below 10⁻³%.

Macroporous anion-exchangers possess a well developed specific surface area. They are characterized by great accessibility of all active centres. Therefore the results the separation of rare earth elements(III) on these anion-exchangers are much better compared with the microporous anion-exchangers. In the studied systems on the anion-ex-

changers Wofatit SBW and SBK, the results of separation were a few times worse. With the increase of cross-linking of Wofatit SBW, a gradual increase of the system effectiveness was observed. The effectiveness of separation increases reaching a maximum at 6% DVB and then decreases which may result from the “sieve effect”, i.e. exclusion of the large ions of Ln(NO₃)_n³⁻ⁿ complexes from the ion-exchange phase.

However, in the case of separation of the Sm(III)–Nd(III) pair, the ion-exchangers Wofatit SBW and SBK proved completely useless, independent of cross-linking, in the systems 90% (v/v) C₃H₇OH–10% 7 M HNO₃.

4. Conclusion

The best results of separation were obtained on the strongly basic anion-exchanger Lewatit MP 5080. This system can be successfully applied to obtain rare earth elements(III), particularly yttrium(III) of great purity on the macro scale.

Table 3
Characterisation of anion-exchangers

Anion-exchangers	Producer	Skeleton structure	Type of functional groups	Grain size mesh	Ion-exch. capacity, meq/cm ³	Bed density, g/cm ³
Wofatit SBW×2%	Veb. Chemikomb. Bitterfeld, Germany	S+DVB	–N ⁺ (CH ₃) ₃	50–100	0.7	0.168
Wofatit SBW×4%	Veb. Chemikomb. Bitterfeld, Germany.	S+DVB	–N ⁺ (CH ₃) ₃	50–100	0.9	0.518
Wofatit SBW×6%	Veb. Chemikomb. Bitterfeld, Germany.	S+DVB	–N ⁺ (CH ₃) ₃	50–100	–	0.330
Wofatit SBW×8%	Veb. Chemikomb. Bitterfeld, Germany	S+DVB	–N ⁺ (CH ₃) ₃	50–100	1.2	0.522
Wofatit SBW×12%	Veb. Chemikomb. Bitterfeld, Germany	S+DVB	–N ⁺ (CH ₃) ₃	50–100	1.2	0.357
Wofatit SBW×16%	Veb. Chemikomb. Bitterfeld, Germany	S+DVB	–N ⁺ (CH ₃) ₃	50–100	0.9	0.634
Wofatit SBK×7%	Veb. Chemikomb. Bitterfeld, Germany	S+DVB	–N ⁺ (CH ₃) ₃	50–100	1.2	0.538
Lewatit MP 5080	Merck, Germany	S+DVB MP	–N ⁺ (CH ₃) ₂ C ₂ H ₄ OH	100–200	1.4	0.323

S+DVB, co-polymer of styrene with divinylbenzene. S+DVB MP, co-polymer of styrene with divinylbenzene with macroporous structure.

It was stated that the strongly basic macroporous anion-exchangers can be regenerated with two to four bed volumes of water after the purification process.

Other advantages of this method are relatively low investment costs as well as simple and cheap regeneration of the anion-exchanger bed.

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