DETERMINATION OF RARE EARTH ELEMENTS BY ION PAIR HPLC WITH POST-COLUMN DERIVATIZATION USING ARSENAZO III

Vlastimil KUBÁŇ[a] and Dimitrii Borisovich GLADILOVICH[b]

[a] *Department of Analytical Chemistry, J. E. Purkyně University, 611 37 Brno, Czechoslovakia and*

[b] *Department of Analytical Chemistry, A. A. Zhdanov University, 199 164 Leningrad, U.S.S.R.*

Received November 5th, 1987
Accepted January 3rd, 1988

Rare earth elements can be determined on a CGC column 3 × 150 mm packed with Separon SGX C 18 modified with sorbed ammonium dodecyl sulfate (from solutions with $c = 5$ mmol l^{-1}) by isocratic or stepwise gradient elution with ammonium DL-α-hydroxyisobutyrate solution (20—160 mmol l^{-1}) at pH 4·5. The method of post-column derivatization with a solution of Arsenazo III (5 μmol l^{-1}) in 0·1M formate buffer at pH 2·9—3·0 for photometric detection enables 10—150 or 6—155 ng of rare earth ions in 10 or 25 μl sample, respectively, to be determined with a reproducibility of 3—5% for 70—90 ng of rare earth ions in sample ($n = 5$—7). By preconcentration on the analytical column from 0·1—2·5 ml sample volumes followed by stepwise gradient elution, 30—80 μg of rare earth ions in 1 ml sample can be determined with a reproducibility of 4% or better, the recovery being 90—106%. The procedures were applied to the determination of rare earth elements in samples of apatite, oxide concentrates and a luminophor, and a very good agreement with the results obtained by optical methods was achieved.

Rapid, still accurate methods for the routine determination of the individual rare earth elements (henceforth REE's) in samples of diverse kind are gaining in importance. REE's can be present in very different proportions, from equimolar to $1 : 10^4$. Among the most important techniques employed for this purpose, in addition to AES, RFA, ICP and AAS, are chromatographic techniques.

The classical procedures of chromatographic separation on strongly acid ion exchangers in the presence of chelating eluting agents such as hydroxy-acids, chelatons, etc., are time consuming[1,2]. Chromatographic methods have become highly effective for the determination of REE's with the introduction of fine-grain styrene–divinylbenzene sorbents and sorbents with chemically bonded phases[3–7].

Among techniques finding ever-increasing application is ion pair chromatography using less expensive sorbents for reverse phase chromatography based on alkylated silica gels. Sorbents with characteristic properties of low or medium capacity ion exchanges, featuring a great flexibility, have been obtained by sorption of a suitable modifier (hydrophobized ions of the type of alkyl sulfonates, alkyl sulfates or other

compounds possessing long alkyl chains) on the surface of hydrophobized silica gel. Among the most widely used modifiers are hexyl, heptyl or octyl sulfonate, dodecyl sulfate and other compounds of this kind[3-17].

Ion pair chromatography has found use for the separation and quantitation of a number of organic ionic compounds and inorganic ions, including REE's and related elements, e.g., for the determination of lanthanoids, yttrium, thorium and uranium in uranium ores[15], minerals and samples with complex matrices[12,13], in geochemical surveying, technological process monitoring[15], as well as in studying some theoretical aspects of HPLC[14,16].

In the present work, the possibility is examined of using a simple chromatographic apparatus including a reaction detector for the separation of some groups of REE's and the whole REE group and quantitation of the individual elements by means of post-column derivatization with Arsenazo III. Ion pair chromatography was applied to samples of apatite, oxide concentrates and a luminophor taking into account the effect of interfering ions in the matrix (Ca, Fe, Al, Th, U, Pb, phosphates). The results are compared with those obtained by optical methods.

EXPERIMENTAL

Chemicals and Apparatus

Stock solutions of REE's in concentrations on the order of 10 mmol l^{-1} in approximately 0·1M-HNO_3 were prepared by dissolving precisely weighed amounts of their nitrates (La, Ce, Pr, Nd, Tb, Ho), oxides (Sm, Er, Tm, Lu, Y) or carbonates (Eu, Gd, Dy, Yb) of reagent grade purity, supplied by Reakhim, Moscow, U.S.S.R. (Tm and Lu oxides were from Fluka, Buchs, Switzerland). The solutions were standardized by chelometric titration using xylenol orange as indicator. Working solutions containing REE's in concentrations of 0·01–1 mmol l^{-1} were prepared by diluting the stock solutions with 0·1M-HNO_3.

Starting solution of Arsenazo III (2,7-bis-[(*o*-arsonophenyl)azo]-1,8-dihydroxynaphthalene-3,6-disulfonic acid, henceforth AA3) in a concentration of 0·2 mol l^{-1} was prepared by dissolving 82 mg of the chemical of chromatographic purity in 50 ml of water. Using a high-purity commercial AA3 preparation (Lachema, Brno), the amount of 82 mg was dissolved in 20 ml of water, the solution was stirred for 30 min with 0·2 g of purified Dowex 50W × 8 cation exchanger (50–100 mesh) in the H^+ form, the latter was filtered off using an S3 glass frit, and the solution was diluted with water to 50 ml. Working solutions of AA3 were obtained by diluting 5 ml of the starting solution and 20 ml of 1M formate buffer pH 2·9–3·0 (46 g of HCOOH + NH_3 in a litre) to 200 ml.

Stock solution of DL-α-hydroxyisobutyric acid (henceforth HIBA) in a concentration of 1·0 mol l^{-1} was prepared by diluting 10·4 g of the solid chemical of reagent grade purity (m.p. 79·0°C; Lachema, Brno) in 100 ml of water, and purified by passing it through a 6 × 200 mm column of Dowex 50W × 8 cation exchanger (50–100 mesh) in the H^+ form. Working solutions of ammonium salt of HIBA (20–160 mmol l^{-1}) were obtained by neutralization of the stock solution of HIBA to pH 4·5 with concentrated ammonia followed by dilution with water.

For the preparation of solution of ammonium dodecyl sulfate (ADS), 5·6674 g of sodium dodecyl sulfate of chemical purity (BDH, Poole, U.K.) was dissolved in 100 ml of water and

allowed to pass at a flow rate of 1 ml min^{-1} through a 6 × 200 mm column of Dowex 50W×8 cation exchanger (50—100 mesh) in the NH_4^+ form. The column was regenerated by passing through it 200 ml of 2M-NH_4NO_3 solution at the same flow rate. The eluate was diluted to 200 ml with water.

CGC chromatographic column 3 × 150 mm packed with Separon SGX C 18 sorbent 5 μm particle size (Tessek, Prague) was washed successively with aqueous methanol (φ = 10%) at the lowest atainable flow rate of 0·01 ml min^{-1} for 8 h, with ADS solution (5 mmol l^{-1}) at a flow rate of 0·1 ml min^{-1} for 2—3 h and, prior to the chromatographic separation, with a solution of HIBA (40 mmol l^{-1}) at a flow rate of 0·4 ml min^{-1} for 30—40 min.

The chromatographic apparatus consisted of a VCM 300 high pressure pump (Development Workshop of the Czechoslovak Academy of Sciences, Prague), a 3 × 50 mm glass precolumn, a stop-flow injector (Laboratorní přístroje, Prague), a CGC column packed with modified Separon SGX C 18 (see above), a reaction detector and a flow-through spectrophotometric detector.

The 3 × 50 mm precolumn, packed with Separon SGX C 18 5 μm particle size or with Silpearl silica gel for TLC 14 μm particle size (Lachema, Brno), served to trap impurities from the mobile phase before its entering the injecting device. The use of this precolumn effected an approximately triple prolongation of the use time of the analytical column (to about 100 hours).

Sample was injected with a graduated microsyringe 10 or 25 μl total volume (Hamilton, U.S.A.) and the stop-flow injector into the mobile phase flowing at a rate of 1 ml min^{-1}.

The post-column reactor[18-23] consisted of a PTFE screen-tee type mixing chamber about 600 nl volume, to which the eluate from the chromatographic column and the AA3 reagent were fed through PTFE capillaries 0·3 mm i.d. (Chemplast, Wayne, U.S.A.) at a flow rate of about 1 ml min^{-1} achieved by hydrostatic pressure. After perfect homogenization, the reaction mixture was fed through a reaction coil 0·3 × 400 mm to an 18 μl flow-through cell of a Spekol 21 single beam spectrophotometric detector connected with K 201 recorder (Carl Zeiss, Jena, G.D.R.). REE's were detected at 660 nm, a wavelength corresponding to the absorption maximum[24] of their chelates with AA3.

Stepwise gradient elution was carried out using a six-way valve with central outlet (Mikrotechna, Prague) serving to switch over the feed of HIBA solutions of different concentrations within the region of 10—160 mmol l^{-1} from reservoirs through PTFE capillaries 0·5 mm i.d., fitted with filters at their ends. Highly dilute sample solutions to be preconcentrated on the analytical column were injected by means of a four-way valve, injecting alternately 0·1—2·5 ml of sample and mobile phase with the aid of the VCM 300 pump.

All measurements were performed at 20 ± 1°C.

Sample Decomposition

Oxide concentrates: 50—100 mg of sample was decomposed[25] in 10 ml of HCl (1 : 10) with 2—3 drops of concentrated H_2O_2, evaporated to a minimal volume and diluted with 0·01M-HNO_3 to 100 ml. The solution was additionally diluted 1 : 25 or 1 : 12·5, and 10—25 μl was injected on column.

For the determination of heavy lanthanoids (Tb — Lu), 0·8—1·0 g of sample was dissolved in 10 ml of HCl (1 : 1) with an addition of concentrated H_2O_2 and evaporated to a minimal volume, 10 ml of HNO_3 (1 : 5) was added and the whole was evaporated gently to dryness. The residue was dissolved in 100 ml of 1M-HNO_3, and 10—25 μl of this solution was injected on column.

Apatite: 50—100 mg of sample and 2 g of Dowex 50W × 8 cation exchanger (50—100 mesh) were shaken with 25 ml of water at approximately 50°C for 3 h, the catex was collected in a column

with a glass frit and washed with 100 ml of water, and the sorbed REE's were eluted with 50 ml of 8M-HNO_3. The eluate was evaporated to a minimal volume and repeatedly dissolved in 10 ml of water and evaporated[26]. The residue was diluted with 0·01M-HNO_3 to 100 ml, and 10–25 μl of sample was injected on column.

Luminophor: 50–100 mg of luminophor (Y_2O_3 with 4% Eu_2O_3) was dissolved in 5 ml of HNO_3 (1 : 1) with an addition of 2–3 drops of concentrated H_2O_2 and evaporated to dryness[27]. The residue was wetted with 5 drops of concentrated HNO_3 and diluted with water to 100 ml. One ml of this solution was diluted with water to 25 ml, and 25 μl sample was injected on column.

Preconcentration on cation exchanger: The desired volume of sample of water at pH ≈ 4 was shaken with Dowex 50W × 8 (50–100 mesh, 20 g per litre of water) for about 2 hours[26]. The latter was collected in a column fitted with a frit, washed with 50 ml of water and 50 ml of 2M-HNO_3, and the REE's were eluted with 50 ml of 8M-HNO_3. The ensuing procedure was as with apatite.

Preconcentration on analytical column: 0·1–2·5 ml of sample solution at pH ≈ 4 was injected on the analytical column (see above) via the four-way valve. Before and after the application of sample, the column was washed with aqueous methanol (φ = 10%) for 10 min. The REE's were eluted in the stepwise gradient mode as described later.

RESULTS AND DISCUSSION

Isocratic Elution

The quality of separation of the individual REE's depends primarily on the concentration of HIBA in the mobile phase and on the acidity of the latter[28]. Under otherwise identical conditions, the retention times increase with lowering pH of the mobile phase and lowering concentration of HIBA in it (Table I).

In general, the REE's can be divided into four groups so that in each group, under suitable experimental conditions, the retention times never exceed 10–15 min. Within each group, the REE's can be perfectly separated by isocratic elution at pH ≈ 4·5 and the following concentrations of HIBA:

1. Yb, Er, Ho, Dy, (Y), Tb: c(HIBA) = 40–60 mmol l^{-1};
2. Dy, (Y), Tb, Gd, Eu, Sm: c(HIBA) = 90 mmol l^{-1};
3. Sm, Nd, Pr: c(HIBA) = 120 mmol l^{-1};
4. Nd, Pr, Ce, La: c(HIBA) = 150 mmol l^{-1}.

Under these conditions, the retention times of the indiviual REE's in each group lie within the limits of 2–7, 3–10, 5–11 and 5–12 min, respectively. The retention times vary only slightly with column ageing; only after 2–3 weeks of performance (100–200 elutions) the relative changes exceed 5%, presumably due to decreasing activity of the modified sorbent.

The perfect separation of REE's in groups 1 and 4 is documented by Figs 1 and 2, respectively; an exception is the Y–Dy pair whose elution curve is insufficiently separated ($R_{ij} \leqq 0{\cdot}2$), the two elements giving rise to a single distorted peak.

TABLE I

Dependence of retention time (t_R, min) of REE on the acidity of eluent and concentration of HIBA in the mobile phase; $m_{REE} = 50-80$ ng V(sample) = 10 µl, pH 4·5 for variable c(HIBA) and c(HIBA) = 90 mmol l^{-1} for variable pH, CGC column 150 × 4·6 mm packed with Separon SGX C 18, ADS modifier. Reproducibility ±0·2, ±0·5 and ±(0·8–1·0) min for $t_R < 6$, $t_R = 6-15$, and $t_R > 15$ min, respectively, for a period of about 2 weeks and for about 100–200 elutions

Ion	c(HIBA), mmol l^{-1}					pH						
	40	60	90	120	150	3·0	3·5	4·0	4·4	4·7	5·1	5·5
Lu	2·9	2·6	2·0	—	—	—	—	—	—	—	—	—
Yb	3·8	2·8	2·2	—	—	13·4	3·2	2·5	2·4	—	—	—
Tm	4·7	3·5	2·4	—	—	—	—	—	—	—	—	—
Er	5·2	4·1	2·5	—	—	23·5	4·9	2·8	2·6	—	—	—
Ho	6·6	5·3	2·7	—	—	32·0	5·9	3·4	2·9	—	—	—
Dy	8·3	6·8	3·0	—	—	42·5	8·5	3·8	3·4	3·0	2·7	—
Tb	11·5	9·2	3·5	—	—	—	11·8	4·9	3·5	3·4	3·0	2·9
Gd	—	14·5	5·5	3·2	3·0	—	22·9	7·3	4·7	4·0	3·5	3·3
Eu	—	—	6·7	3·8	3·3	—	30·3	9·2	5·8	4·6	3·8	4·0
Sm	—	—	9·5	4·7	3·5	—	—	12·5	8·0	5·3	4·3	4·4
Nd	—	—	15·8	8·9	5·0	—	—	—	16·5	8·9	6·5	6·1
Pr	—	—	19·5	11·0	5·9	—	—	—	21·0	10·7	7·7	7·4
Ce	—	—	—	14·5	7·4	—	—	—	—	13·5	9·5	9·0
La	—	—	—	21·5	11·3	—	—	—	—	21·2	14·0	13·5

The calibration plots of peak heights vs REE concentrations are linear over the region of 10–150 ng REE in the injected volume (10 or 25 μl). Reproducibility is 3–5% for 70–90 ng REE in sample ($n = 5-7$), which corresponds to limits of determination, defined by the criterion of $10s_0$, where s_0 is the standard deviation estimate for the noise of the recording device, within the region of 0·6–2·8 ng REE in sample[29].

Fe(III) and Al(III) ions are eluted in the isocratic mode within 2 min after injection (Fig. 3). The former ions interfere only exceptionally, for the most easily eluted REE's (Table I) and in a 100–200-fold excess. Al(III) and Ca(II) ions give no coloured products with AA3 up to a 100-fold or 200-fold excess, respectively, so that they do not interfere with the detection in the visible spectral region. At higher concentrations of Al(III), a weak peak can appear immediately after sample injection (Fig. 3). Th(IV) and U(VI) ions give a very disperse peak over the region of peaks of Yb–Ho, and up to a 10-fold concentration excess do not interfere with the determination of REE's. Removed during the sample treatment, phosphate ions do not interfere.

Within the various groups, the REE ions do not affect each other unless the excess of ions with a longer retention time with respect to ions with a shorter retention time

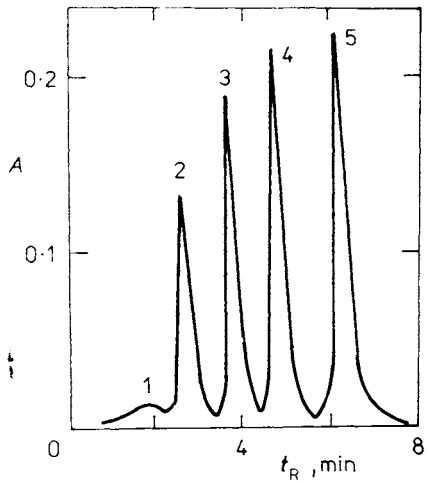

FIG. 1

Chromatographic separation of 88·04 ng Er(III), 88·77 ng Yb(III), 84·36 ng Ho(III), and 83·2 ng Dy(III) in 10 μl sample by isocratic elution with HIBA solution (60 mmol l^{-1}) at pH 4·5. Peaks: 1 impurities (Fe, Al), 2 Yb, 3 Er, 4 Ho, 5 Dy

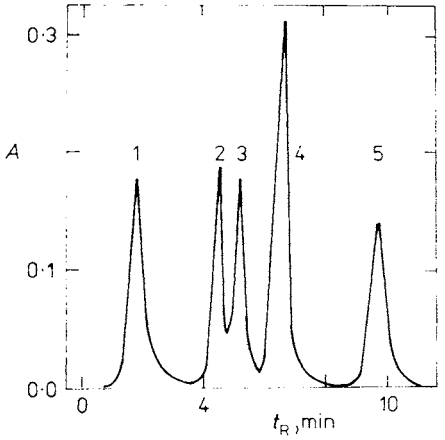

FIG. 2

Chromatographic separation of 72·7 ng Nd(III), 70·1 ng Pr(III), 142·1 ng Ce(IV), and 69·0 ng La(III) in 10 μl sample by isocratic elution with HIBA solution (150 mmol l^{-1}) at pH 4·5. Peaks: 1 impurities, 2 Nd, 3 Pr, 4 Ce, 5 La

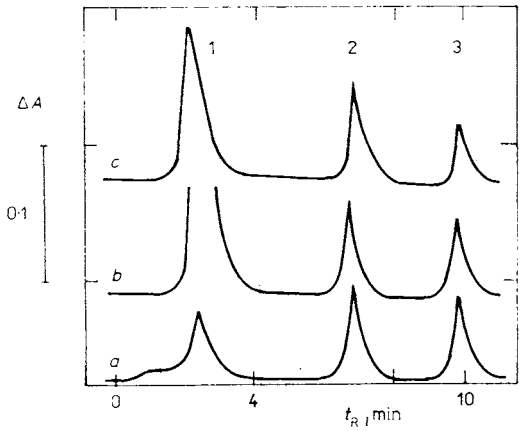

FIG. 3

Chromatographic separation of 28·4 ng Ce(IV) and 27·6 ng La(III) from *a* 100 mg Ca(II), *b* 220 mg Fe(III) and *c* 110 mg Al(III) in 10 μl sample by isocratic elution with HIBA solution (150 mmol l^{-1}) at pH 4·5. Peaks: 1 Ca or Fe or Al, 2 Ce, 3 La

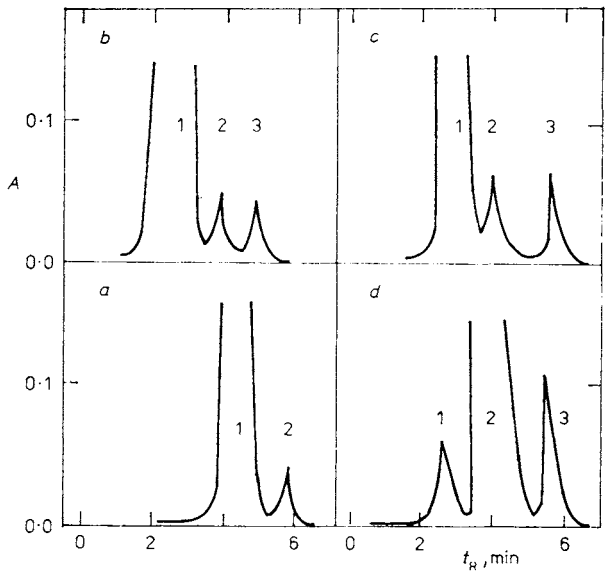

FIG. 4

Determination of trace concentrations of REE in the presence of high concentration excess of other REE with shorter retention times (*a*—*c*) and determination of approximately 4% Eu in Y_2O_3 based luminophor (*d*) in 10 μl samples by isocratic elution with HIBA solutions, c = = 60 mmol l^{-1} (*a*, *b*), c = 90 mmol l^{-1} (*c*, *d*) at pH 4·5. *a* 8·4 ng Ho(III) in the presence of 880 ng Er(III); *b* 8·4 ng Ho(III) and 16·4 ng Er(III) in the presence of 444 ng Yb(III), *c* 13·7 ng Sm(III) and 15·9 ng Eu(III) in the presence of 6·7 mg Y(III), *d* 101·7 mg sample, dilution 1 : 10. Peaks: *a* 1 Er, 2 Ho; *b* 1 Y, 2 Er, 3 Ho; *c* 1 Y, 2 Eu, 3 Sm; *d* 1 unknown, 2 Y, 3 Eu

exceeds 1 000 : 1. The latter ions do not interfere with the determination of the former ions unless their excess is higher than 1 000 : 1 and the retention time difference is shorter than 2 min, whereas if the retention time difference is about 1 min or 0·5 min, the excess must not excess 50 : 1 and 5 : 1, respectively, as indicated by results presented in Fig. 4 and in the later text.

Stepwise Gradient Elution

For a better separation of the whole group of REE's, stepwise gradient elution was employed making use of the pronounced dependence of the retention times on the acidity of the mobile phase and on the concentration of HIBA (ref.[24]). This stepwise gradient mode was accomplished by means of the six-way valve with central outlet. It was ascertained that the time elapsed from the change in conditions at the analytical column inlet to the change of the analytical signal in the detector is 6–7 min.

The best results were obtained by eluting with HIBA in concentrations of 40 mmol . $.l^{-1}$ up to 5 min, 80 mmol l^{-1} in 5–15 min and 160 mmol l^{-1} after 15 min. The chromatogram for the entire REE group is shown in Fig. 5. The separation is perfect except for the Y–Dy pair whose peak remains unresolved ($R_{ij} \leqq 0{\cdot}4$).

The calibration plots of chromatographic peak heights are linear over the region of 6–155 ng REE in 10 or 25 µl sample. The corresponding statistical parameters are given in Table II. The differences of the y-intercepts from zero are statistically insignificant.

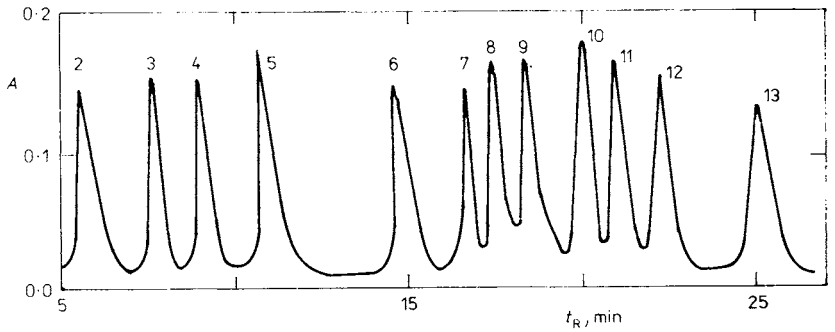

FIG. 5

Chromatographic separation of 133·2 ng Yb(III), 123·1 ng Er(III), 126·5 ng Ho(III), 124·8 ng Dy(III), 79·1 ng Tb(III), 77·1 ng Gd(III), 79·7 ng Eu(III), 68·2 ng Sm(III), 72·7 ng Nd(III), 70·1 ng Pr(III), 71·0 ng Ce(IV), and 69·0 ng La(III) in 10 µl sample by stepwise gradent elution with HIBA solutions, c = 40 mmol l^{-1} (<5 min), 80 mmol l^{-1} (5–15 min), and 160 mmol l^{-1} (>15 min) at pH 4·5. Peaks: **2** Yb, **3** Er, **4** Ho, **5** Dy, **6** Tb, **7** Gd, **8** Eu, **9** Sm, **10** Nd, **11** Pr, **12** Ce, **13** La

Fe(III) and Al(III) ions are eluted at short retention times and do not interfere with the determination up to a 1 000-fold and 10 000-fold excess, respectively. Ca(II) and Pb(II) ions do not interfere up to a 10 000-fold excess, Th(IV) and U(VI) ions give rise to a disperse peak over the region of Yb – Ho peaks and do not interfere up to a 20-fold concentration excess.

TABLE II

Statistical parameters of the calibration dependence of chromatographic peak height on concentration for the stepwise gradient elution of REE; $m_{REE} = 6-155$ ng, V(sample) = 10 µl, c(HIBA) = 40–160 mmol l^{-1}, pH 4·5

Ion	b^a	$s_{xy}{}^b$	$s_b{}^c$	DL^d	Ion	b^a	$s_{xy}{}^b$	$s_b{}^c$	DL^d
Yb	0·421	2·64	0·016	5·8	Er	0·481	2·52	0·016	4·5
Ho	0·479	1·44	0·010	2·6	Dy	0·461	3·20	0·020	6·1
Tb	0·608	3·75	0·025	4·9	Gd	0·554	2·00	0·020	4·2
Eu	0·618	4·05	0·027	5·5	Sm	0·624	4·02	0·031	6·0
Nd	0·556	1·45	0·010	2·1	Pr	0·470	3·60	0·027	6·1
Ce	0·579	3·55	0·027	4·6	La	0·576	4·08	0·031	4·9
Y	1·073	1·23	0·016	0·9					

[a] Slope of the calibration straight line $y = a + bx$; [b] standard deviation estimate of dispersion about the regression straight line; $r_{xy} = 0{\cdot}9987 - 0{\cdot}9999$, $a < 0{\cdot}006$; [c] standard deviation estimate for slope b; [d] determination limit, DL = $10s_0$ (in ng per 10 µl), where s_0 is the standard deviation estimate for the recording device noise.

TABLE III

REE recovery from analytical column preconcentration; $m_{REE} = 30-80$ ng, c(HIBA) = 20 to 160 mmol l^{-1}, pH 4·5, stepwise gradient elution

Ion	n^a	R^b, %	s^c	Ion	n^a	R^b, %	s^c
Yb	5	96 ± 9	7·1	Er	5	104 ± 8	6·8
Ho	5	98 ± 8	6·5	Dy	5	100 ± 7	6·0
Tb	3	104 ± 16	6·5	Gd	3	111 + 13	5·0
Eu	3	91 ± 25	10·2	Sm	3	106 ± 15	5·9
Pr	8	97 ± 23	9·2	Nd	8	98 ± 19	7·7
Ce	8	97 ± 4	2·5	La	8	94 ± 10	11·9
Y	8	101 ± 7	6·5				

[a] Number of determinations; [b] recovery, $R = 100 \cdot c_{exp}/c_{theor}$; [c] standard deviation of the mean

REE *Preconcentration*

It follows from a comparison of the REE preconcentration procedures on the CGC Separon SGX C 18 column and the Dowex 50W × 8 cation exchanger that both enable 30 – 80 μg REE in 1 ml sample solution to be determined with a reproducibility of 4% and recovery of 90 – 106% (Table III) for standard REE mixtures in the above concentration range. The recovery confirms negligible losses of the individual REE's during the operations associated with the preconcentration, separation and detection.

From the point of view of results obtained, the procedure where the REE's are preconcentrated directly on the analytical column is comparable to that where the ions are preconcentrated on a cation exchanger, and in rapidity and simplicity of operation the former is superior to the latter. Partial separation of interfering ions on an ion exchanger column may be convenient for samples with complex matrices and high concentrations of interferents.

TABLE IV

Results of determination of Nd, Pr, Ce, and La in apatite and oxide concentrate samples by isocratic elution; c(HIBA) = 150 mmol l^{-1}, pH 4·5

Ion	w^a, wt. %	s^b	w^c, wt. %	s^c
	A: Apatite, m = 58·3 mg, V = 20 μl, n = 8			
Nd	0·117 ± 0·08	0·67	0·117 ± 0·007	0·016
Pr	0·057 ± 0·012	1·00	0·041 ± 0·008	0·002
Ce	0·346 ± 0·026	2·07	0·339 ± 0·01	0·022
La	0·249 ± 0·023	1·89	0·24 ± 0·01	0·024
	B: Oxide concentrate, m = 60·8 mg, V = 10 μl, n = 11			
Nd	11·5 ± 0·6	0·9	15·8 ± 0·6	—
Pr	4·0 ± 0·8	0·8	4·54 ± 0·19	—
Ce	28·9 ± 1·1	1·6	32·3 ± 1·5	—
La	15·6 ± 1·1	1·1	20·6 ± 1·0	—
	C: Oxide concentrate, m = 66·6 mg, V = 10 μl, n = 10			
Nd	9·7 ± 0·7	0·9	10·0 ± 0·7[d]	—
Pr	4·6 ± 0·6	0·9	4·5 ± 0·2[d]	—
Ce	36·7 ± 1·3	1·9	37·3 ± 0·6[d]	—
La	20·6 ± 1·6	1·6	21·1 ± 0·8[d]	—

[a] $w \pm tsn^{-1/2}$; [b] standard deviation of the mean; [c] arithmetic mean of interlaboratory assay, results of RFA, AAS, ICP, and AES, ref.[25] (n = 18); [d] spectrophotometric determination, n = 8.

Application to Actual Samples

The perfect separation of REE's in groups by isocratic elution was made use of for working out methods for the determination of Nd(III), Pr(III), Ce(IV), and La(III) as the majority components in samples of apatite and oxide concentrates (Fig. 6) and the determination of Eu(III) in Y_2O_3-based luminophors doped with approximately 4% Eu_2O_3 (Fig. 4*d*).

Sample solutions in volumes of 10–25 μl (apatite, oxide concentrates) or 10 μl (luminophors) were injected and HIBA solution (150 or 90 mmol l^{-1}) at pH 4·5 with 0·1 mmol l^{-1} ADS was used for separation. The results of determination are given in Table IV and compared with the arithmetic means of results obtained by optical methods[25] (AES, RFA, ICP, AAS) and MAS in an interlaboratory assay. A very good agreement was obtained for the vast majority of data. Only for Nd(III) and La(III) in sample B the results obtained by IP HPLC are lower than the means of values obtained by other methods, still they lie within ranges of the optical methods data.

The results of direct determination of Eu(III) in luminophors (Fig. 4) for three sample amounts (101·7, 51·4, and 58·3 mg) and those obtained using the method of standard addition of 3·98 ng Eu to each volume injected, differ but slightly (3·98 ± 0·22, 4·17 ± 0·15, and 4·12 ± 0·09%) and the average value of 4·00 ± 0·10% (n = 15, s_r = 7·1%) agrees very well with that obtained by AES, viz[26] 4·05%.

The stepwise gradient elution mode was used for medium heavy and heavy REE's in oxide concentrates, where their content did not exceed 1%; injected were 10–25 μl volumes of solutions obtained by dissolving higher amounts (0·8–1·0 g) of sample.

In the Sm, Eu, Gd, Y, Dy and the Tb–Lu groups, the elements are separated perfectly except for the Dy–Y pair. The results of determination are given in Table V

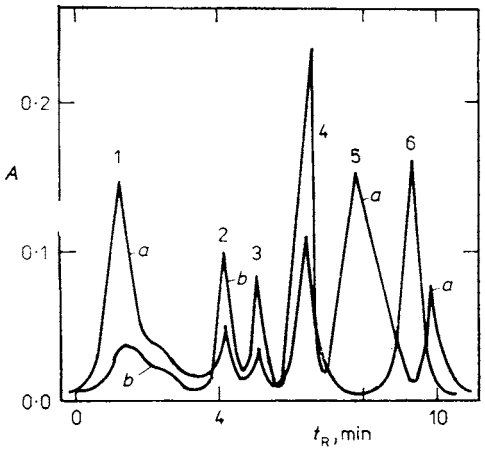

FIG. 6

Determination of REE in samples of apatite (*a*) and oxide concentrate (*b*) by isocratic elution with HIBA solution (150 mmol l^{-1}) at pH 4·5. *a* 58·3 mg sample, 20 μl; *b* 66·6 mg sample, method of standard addition of 14·5 ng Nd(III), 35·05 ng Pr(III), 14·3 ng Ce(IV), 27·6 ng La(III) per 20 μl sample. Peaks: 1 Al, Fe, 2 Nd, 3 Pr, 4 Ce, 5 unidentified, 6 La

along with those obtained by optical methods[25-27]. The agreement between the two sets of data is very good for the vast majority of elements. The Dy + Y content was determined as a sum, the two elements giving together a single distorted peak. In addition, peaks of Lu(III) and Tm(III) in 0·001% concentrations were identified.

The method of preconcentration of REE's from large volumes on the analytical column was applied to samples of apatite and oxide concentrates, where their contents did not exceed 0·01%. The results of determination, along with those obtained by optical methods[25,26], are given in Table VI. The agreement of the results is good, only for some REE's the HPLC data are several units per cent lower than the averages of results obtained by the optical methods, still remaining, however, within their ranges.

In conclusion, ion pair chromatography on a column with a sorbent based on alkylated silica gel with a sorbed modifier of alkyl sulfate or alkyl sulfonate type shows great promise for the quantitation of the whole group of REE's as well as of the individual elements in samples of diverse kind. Chromatographic separation can be applied even if the concentrations of the individual REE's differ by several

TABLE V

Results of determination of some REE in oxide concentrate samples by stepwise gradient elution; m_{REE} = 10–150 ng, V(sample) = 10–25 µl, c(HIBA) = 40–160 mmol l^{-1}, pH 4·5, m(sample) = 50–100 mg (sample B), 800–1 000 mg (sample C)

Ion	w^a, wt. %	s^b	w^c, wt. %
	Sample B		
Gd	1·41 ± 0·10	0·14	1·28 ± 0·22
Eu	0·63 ± 0·06	0·09	0·54 ± 0·04
Sm	1·77 ± 0·23	0·18	2·14 ± 0·09
Y + Dy	1·11 ± 0·03	0·05	1·28 ± 0·06
Yb	0·034 ± 0·009	0·006	0·028
Er	0·110 ± 0·010	0·009	0·12 ± 0·03
Ho	0·102 ± 0·007	0·011	0·13 ± 0·03
Tb	0·065 ± 0·005	0·010	0·062 ± 0·013
	Sample C		
Gd	0·329 ± 0·022	0·027	—
Eu	0·23 ± 0·04	0·042	—
Sm	0·85 ± 0·04	0·007	
Y + Dy	0·157 ± 0·02	0·024	—

[a-c] See Table IV.

orders of magnitude and if interferents are present in concentrations exceeding multiply those of the REE's. Additional improvement in selectivity could be achieved by using masking agents in mixture with the organic analytical reagent for the post-column derivatization[24].

TABLE VI

Results of determination of some REE in apatite (sample A) and oxide concentrates (samples B, C) after preconcentration on a CGC column packed with ADS-modified Separon SGX C 18; V(sample) = 1–2·5 ml, c(HIBA) = 40–160 mmol l^{-1}, pH 4·5, m(sample) = 800–1 000 mg

Ion	n	$w \cdot 10^3$, wt. %[a]	$s \cdot 10^{3b}$	$w \cdot 10^3$, wt. %[c]
		Sample A		
Yb	2	≦1	—	—
Er	3	1·7 ± 0·6	0·25	≦2
Tm	2	≦0·5	—	—
Ho	3	1·1 ± 0·4	0·19	≦1
Y(Dy)	4	15·1 ± 0·14	9	29·3 ± 1·1
Tb	3	1·1 ± 0·9	0·3	—
Gd	4	9·4 ± 0·1	1·3	11·3 ± 0·4
Eu	4	4·6 ± 1·2	0·7	4·4 ± 0·3
Sm	4	13·9 ± 1·1	0·7	20·0 ± 0·3
		Sample B		
Er	4	129 ± 17	11	120 ± 30
Ho	4	96 ± 17	11	130 ± 30
Tb	5	117 ± 13	10	62 ± 13
Gd	5	1 160 ± 220	180	1 280 ± 220
Eu	5	520 ± 50	53	540 ± 40
Sm	5	1 450 ± 300	120	2 140 ± 90
		Sample C		
Yb	3	1·5	—	—
Er	4	4·7 ± 0·5	—	—
Ho	4	3·0 ± 0·4	—	—
Y(Dy)	3	9·6 ± 1·0	—	—
Tb	4	240 ± 40	34	—
Gd	5	42 ± 6	51	—
Eu	5	27 ± 4	30	—
Sm	5	95 ± 8	30	

[a–c] See Table IV; n is the number of determinations.

The limit of determination can be increased, with a sustained or only slightly poorer reproducibility of measurement, by preconcentration of the REE's from highly dilute solutions on the analytical column; the recovery is 100 ± 10%.

The authors wish to thank Dr V. Radil of the Institute of Nuclear Fuels in Prague-Zbraslav for supplying them with a sample of chromatographically pure Arsenazo III.

REFERENCES

1. Ryabchikov D. I., Ryabukhin V. A.: *Analiticheskaya khimiya redkozemelnykh elementov i ittriya.* Nauka, Moscow 1966.
2. Procházka M.: *Thesis.* Charles University, Prague 1985.
3. Takata Y., Arikawa Y.: Bunseki Kagaku *24*, 762 (1975).
4. Dubuquoy C., Meker G.: Analusis *5*, 314 (1977).
5. Larsen N. R.: J. Radioanal. Chem. *52*, 85 (1979).
6. Elchuk S., Cassidy R. M.: Anal. Chem. *51*, 1434 (1979).
7. Mazzucotelli A., Dadone A., Frache R., Baffi F.: J. Chromatogr. *349*, 137 (1985).
8. Mazzucotelli A., Dadone A., Frache R., Baffi F.: Chromatographia *15*, 697 (1982).
9. Cassidy R. M., Elchuk S.: J. Chromatogr. Sci. *18*, 217 (1980).
10. Cassidy R. M., Elchuk S.: J. Liq. Chromatogr. *4*, 379 (1981).
11. Cassidy R. M., Elchuk S.: Anal. Chem. *54*, 1558 (1982).
12. Knight C. H., Cassidy R. M., Rocoskie B. M., Green L. W.: Anal. Chem. *56*, 474 (1984).
13. Cassidy R. M., Elchuk S., Elliot N. L., Green L. W., Knight C. H., Rocoskie B. M.: Anal. Chem. *58*, 1181 (1986).
14. Cassidy R. M., Fraser M.: Chromatographia *18*, 369 (1984).
15. Barkley D. J., Blanchette M., Cassidy R. M., Elchuk S.: Anal. Chem. *58*, 2222 (1986).
16. Cassidy R. M., Miller F. C., Knight C. H., Roddick J. C., Sullivan R. W.: Anal. Chem. *58*, 1389 (1986).
17. Elliot N. L., Green L. W., Rocoskie B. M., Cassidy R. M.: Anal. Chem. *58*, 1178 (1986).
18. Cassidy R. M., Elchuk S., Dasgupta P. K.: Anal. Chem. *59*, 85 (1987).
19. Krull I. S. (Ed.): *Reaction Detectors in Liquid Chromatography*, p. 5. Academic Press, New York 1987.
20. Cassidy R. M., Karcher B. D.: J. Chromatogr. Sci. *34*, 129 (1986).
21. Frei R. W.: Chromatographia *15*, 161 (1982).
22. Deelder R. S., Kuijpers A. T. J. M., Van den Berg J. H. M.: J. Chromatogr. *255*, 545 (1983).
23. Jansen H., Brinkman U. A. T., Frei R. W.: J. Chromatogr. Sci. *23*, 279 (1985).
24. Gladilovich D. B., Kubáň V., Sommer L.: Talanta, *35*, 259 (1988).
25. Šulcek Z., Weiss D.: *Stanovení sumy vzácných zemin a thoria v apatitových koncentrátech. Report.* Central Geological Institute, Prague 1986.
26. Otruba V.: Private communication.
27. Weiss D.: Chem. Listy *79*, 205 (1985).
28. Kubáň V., Sommer L., Gladilovich D. B.: Zh. Anal. Khim., in press.
29. Sommer L., Ackermann G.: Pure Appl. Chem. *58*, 1015 (1986).

Translated by P. Adámek.