

CHROMATOGRAPHIC BEHAVIOUR OF LIGHT RARE EARTHS ON ANION-EXCHANGE PAPER IN NITRATE-METHANOL SYSTEMS

E. CERRAI AND C. TRIULZI

*Laboratori C.I.S.E., Segrate, Milan (Italy)**

(Received March 11th, 1964)

The use of inorganic acid-alcohol media for adsorption of inorganic ions on anion-exchange resins has been described earlier in the literature.

Owing to the tendency shown by several elements to form negatively charged chloro-complexes which are more or less adsorbed by strong anion-exchange resins, chloride-alcohol systems are the ones that have been most extensively investigated. The application of such chloride-alcohol media to anion-exchange separations was reported by WILKINS AND SMITH¹ as well as by FRITZ AND PIETRZYK².

KORKISCH and co-workers³ have recently shown that in a nitric acid medium the adsorption of rare earths on a strong-base anion-exchange resin can be considerably enhanced by the presence of an aliphatic alcohol in the acidic nitrate solution. Generally, at the same acidity, the higher the alcohol concentration the higher is the adsorption of the element. Furthermore, a certain selectivity between the different rare earths in the methanol-HNO₃ system has been shown to occur (especially in the low atom number group) by FARIS AND WARTON⁴, which is practically absent when pure nitric acid is used as the eluent.

In the present work the possibility was investigated of exploiting such selective adsorption for a chromatographic separation of light rare earths on paper.

In analogy with the adsorption of rare earths from nitrate-nitric acid solutions on strong anionic resins, the chromatography of some lanthanides on paper treated with a liquid anion exchanger has already been studied in this laboratory⁵. Therefore an attempt was first made to use paper strips treated with a solution of tri-*n*-octylamine (TNOA)-cyclohexane as the chromatographic support in conjunction with an eluent formed by a methanol-nitric acid mixture. Unfortunately, the TNOA-treated paper strips, which normally behave like a thin layer of an anionic resin with pure inorganic eluents, could not be applied to chromatographic elution with mixed solvents. Some preliminary experiments, in which the R_F of europium was determined on a 0.1 M TNOA-treated paper eluted with 80 % vol. methanol-HNO₃ mixtures, showed that the spots were irregular and that part of the amine was eluted from the paper by the methanol thus giving higher R_F 's than were obtained with untreated paper. A comparison of such values is given in Table I.

Furthermore, liquid-liquid extraction experiments with radioactive tracer europium had shown that no extraction of the element occurred in the organic phase

* Address: C.I.S.E., Casella Postale 3986, Milano, Italy.

TABLE I

COMPARISON BETWEEN R_F OF EUROPIUM ON UNTREATED WHATMAN NO. 1 STRIPS AND THAT ON THE SAME PAPER PRE-TREATED WITH 0.1 M TNOA-CYCLOHEXANE
Ascending elution with 80 % vol. methanol- HNO_3 mixtures.

Nominal HNO_3 molarity	1.2	1.8	2.4	3.0	Observations
Untreated paper	0.53	0.56	0.54	0.59	Regular spots
TNOA-treated paper	0.79	0.72	0.76	0.73	Irregular spots

(0.35 M TNOA-cyclohexane) from a mixture of 3 M HNO_3 -methanol also with a high alcohol content.

It was thus concluded that unlike the case of nitrate- HNO_3 systems, TNOA-treated papers were of no use for chromatography of rare earths with methanol- HNO_3 eluents.

Therefore a support more like an anion-exchange resin, with an inherently greater stability, was chosen, namely, Whatman diethylaminoethyl-cellulose paper DE-20, which is a cellulose anion exchanger where the amine groups are chemically bonded to the cellulose matrix.

A systematic study of HCl-alcohol systems for inorganic chromatography on cellulose ion exchangers (among them DE-20) was recently reported by LEDERER AND MOSCATELLI⁶. Diethylaminoethyl-cellulose paper was also applied by ARNOLD AND RITCHIE⁷ to the separation of rare earths in citrate medium.

EXPERIMENTAL

Reagents, equipment and procedure

The rare earths (nitrates and oxides) were supplied by Fluka (Switzerland) and Light's (London). The required amount was dissolved in the minimum volume of conc. HNO_3 and then carefully dried. Afterwards, 0.15 M HNO_3 was added to obtain solutions containing about 3 mg of each element per ml. The following rare earths were used: La(57), Ce(58), Pr(59), Nd(60), Sm(62), Eu(63), Gd(64), Tb(65), Dy(66), Ho(67), Er(68), Yb(70) and Lu(71). Some preliminary experiments showed that a satisfactory selectivity was only attainable for light rare earths and thus the detailed investigation was confined to the group from La to Gd.

The spots were detected with a 1 % solution of 8-hydroxyquinoline dissolved in a 50/50 (vol.) water-ethanol solution. Experiments on ion-exchange paper (DE-20, Whatman) were carried out on 107 × 225 mm sheets in which fourteen 85 mm long, 13 mm wide parallel strips had been cut. Some reference experiments were performed with Whatman No. 1 CRL/1 type pure cellulose sheets, formed into twelve strips.

Ascending elution with methanol- HNO_3 mixtures was adopted and a tightly closed jar (18 cm × 10 cm diam.) was used fitted with a support for a chromatographic sheet folded to form a cylinder.

Spots of 0.01 to 0.02 ml of solution (30 to 60 μg of the element) were deposited on the paper with a micropipette. In multiple chromatograms, a period of about 30 min was required for the front to move about 8.5 cm and with single (2 × 20 cm) strips about 60 min for a 16 cm run.

The anion-exchange paper is normally supplied in the free base form and results depend on whether or not the paper has been previously treated and, in the latter case, on the way of treatment. Prior to investigating any other item an appropriate method of treatment was checked.

Selection of the pre-treatment procedure of DE-20 paper

The method used for pre-treatment of DE-20 paper appeared to influence both selectivity within the light rare-earth group and general behaviour of the chromatograms, such as spot shape and front regularity. As an index of selectivity, for each sheet obtained with a different treatment method, it was decided to compare results represented by the relationship of the R_F 's as functions of the atomic number (eluent: 3 M HNO₃-80 % vol. methanol) with the theoretical relationship which can be expected with the highest selectivity for rare earths from La to Gd. Since the relationship between experimental R_F 's and atomic number was found sufficiently linear for these rare earths, the theoretical correlation of maximum selectivity is obviously represented by a straight line which passes through $R_F = 0$ for La(57) and $R_F = 1$ for Gd(64) thus having a null intercept and a 0.143 slope.

As for the general appearance of the chromatograms it was decided to reject cases in which spots were badly shaped and the front line seriously affected.

Eight possibilities were explored, they are:

- (1) Paper in the free base form as supplied;
- (2) Paper eluted with 0.1 M NaOH (12 h), then with 0.1 M NaNO₃ (12 h) and finally washed 2 min in distilled water;
- (3) Paper eluted with 0.3 M HNO₃ (30 min) and washed as above;
- (4) *Idem* with 0.3 M NaNO₃ (30 min) and washed;
- (5) *Idem* with 0.3 M NaOH (30 min) and washed;
- (6) Paper washed in 1 M HNO₃ (15 sec), repeated with fresh 1 M HNO₃ (15 sec) and final washing in distilled water for 30 sec;
- (7) As (6), but using 1 M NaNO₃ for the two washings;
- (8) As (6), but using 1 M NaOH for the two washings.

Results are given in Table II, in which the intercepts and slopes of the relationship between experimental R_F 's and atomic numbers are reported for rare earths from La

TABLE II

EFFECT OF PRE-TREATMENT OF DE-20 ON EXPERIMENTAL RESULTS IN ELUTION OF RARE EARTHS La to Gd WITH 3 M HNO₃-80 % VOL. METHANOL MIXTURES
CRL/1 pure cellulose paper after the same treatment is given for comparison.

Treatment	Intercept		Slope		Observations
	DE-20	CRL/1	DE-20	CRL/1	
1	0.13	0.67	0.010	0	Regular spots, irregular solvent front
2	0.16	0.67	0.052	0	Paper became very brittle, poor reproducibility
3	0.12	0.65	0.065	0	Regular spots and solvent front
4	0.14	0.70	0.062	0	Regular spots, slightly irregular solvent front
5	0.13	0.72	0.066	0	Regular spots, very irregular front
6	0.10	0.59	0.054	0	Very regular spots and solvent front
7	0.12	0.68	0.058	0	Regular spots, irregular front
8	0.18	0.68	0.056	0	Very irregular spots and solvent front

to Gd eluted with 3 M HNO₃-80 % vol. methanol on DE-20 paper. Results for elutions on Whatman No. 1, CRL/1 pure cellulose paper after the same kind of pre-treatment are also given for comparison.

From the results given in Table II it can be concluded that in the HNO₃-methanol system pure cellulose paper does not exhibit selectivity for the different rare earths (slope = 0) and R_F values range from 0.59 to 0.72 depending upon the kind of treatment. The anion-exchange paper DE-20 generally has sufficient selectivity for the different rare earths of the La to Gd group, but the reliability of the chromatograms depends on the pre-treatment. From these results three kinds of treatment were shown to be sufficiently satisfactory, namely numbers 3, 4 and 6. Due to the rapidity of treatment and regularity of results, method 6 was chosen for the work described throughout this paper. This consists of two 15 sec washes with 1 M HNO₃ and a 30 sec wash in water, followed by drying in a current of warm air, and will be referred to as the "standard pre-treatment of paper".

Effect of HNO₃ molarity and of methanol concentration

The effect of the nominal molarity of HNO₃ and concentration of methanol in the eluent was investigated by measuring the R_F values on DE-20 paper as a function of atomic numbers of the rare earths from La to Gd for different molarities of HNO₃.

Elutions on DE-20 paper, previously treated by the standard method, were performed with HNO₃ of the following molarities 0.6, 1.2, 2.4 and 3. The plots of R_F vs. atomic number are reported in Figs. 1-4. In each plot a family of curves indicates results at different methanol percentages. Percentage of alcohol and nitric acid molarity are both referred to the total volume of the eluent mixture.

In the four figures, it is shown that pure nitric acid, whatever its molarity from 0.6 to 3 M, yields high R_F values (*i.e.* poor adsorption of the elements) without any selectivity between the different rare earths (horizontal straight line). The presence of

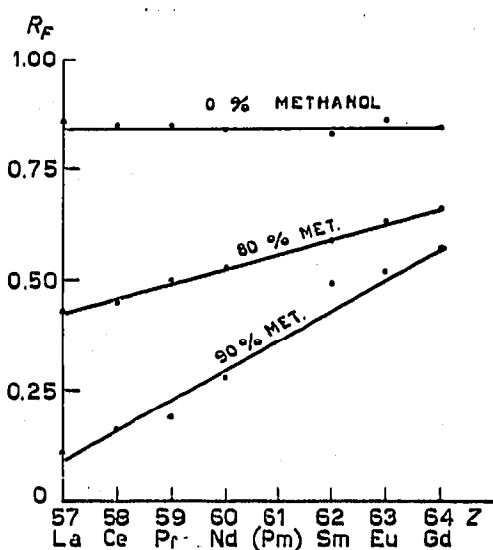


Fig. 1. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with 0.6 M HNO₃ containing methanol at the percentage indicated on the plots.

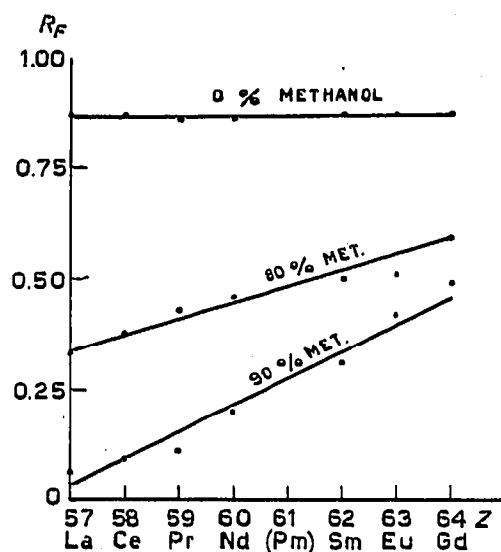


Fig. 2. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with 1.2 M HNO₃ containing methanol at the percentage indicated on the plots.

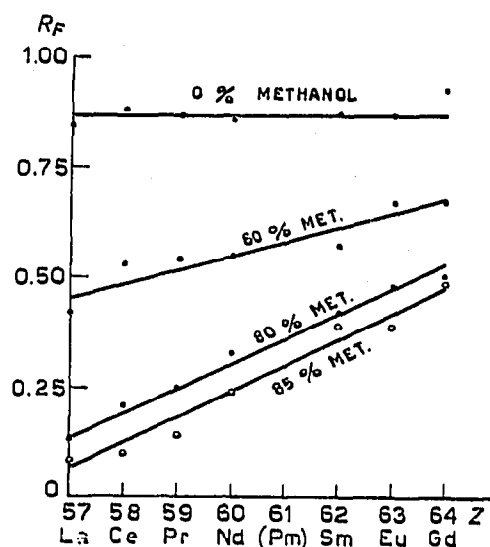
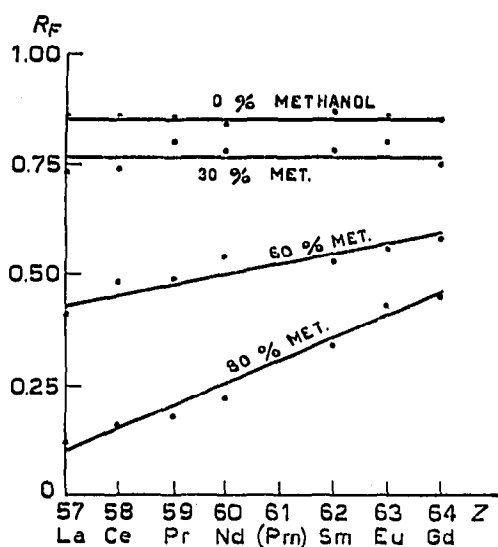


Fig. 3. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with 2.4 M HNO_3 containing methanol at the percentage indicated on the plots.

Fig. 4. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with 3.0 M HNO_3 containing methanol at the percentage indicated on the plots.

methanol increases both adsorption and selectivity which are higher the higher the alcohol percentage. In conditions in which selectivity occurs the elements are less adsorbed the higher the atomic number. In the range of a high alcohol percentage, an increase of the acid molarity is generally beneficial as shown in Figs. 5 and 6 in which the plots of R_F vs. atomic number are reported respectively for 90% and 95% alcohol at different HNO_3 molarities below 1.2 and 0.6 M. In each of the two plots both

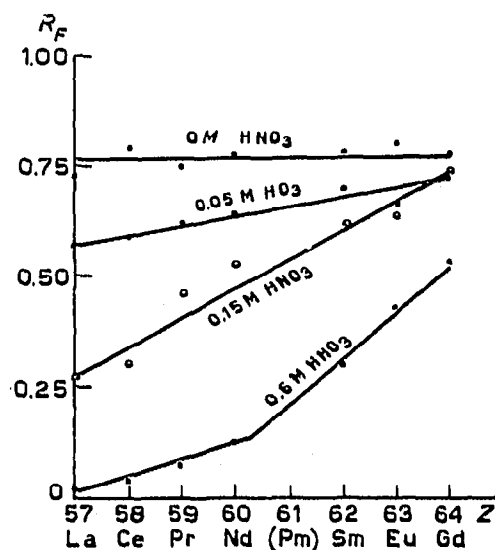
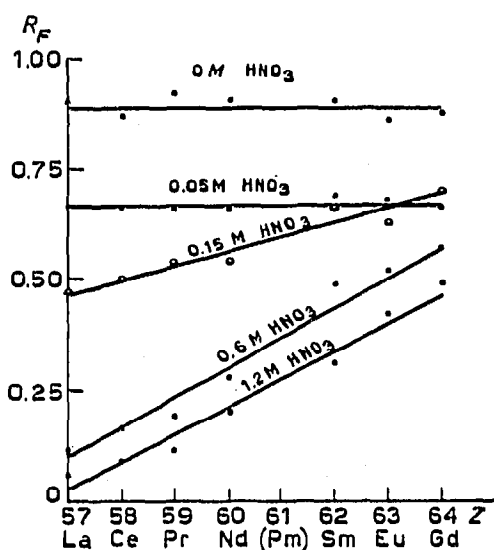


Fig. 5. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with HNO_3 of the molarities quoted containing 90% methanol.

Fig. 6. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with HNO_3 of the molarities quoted containing 95% methanol.

selectivity and adsorption increase with the acid molarity. Due to the improvement attained on changing from 90 % to 95 % methanol-HNO₃ elutions, as shown by a comparison of plots on Fig. 5 with those on Fig. 6, the range of very high alcohol concentrations was further investigated. Thus, elutions with more than 99 % alcohol and very small amounts of 15 M HNO₃ were performed. On the basis of the amount of acid added and of the total volume of the mixture, the molarities of HNO₃ were 0.015, 0.05 and 0.15 M. Results are given in Fig. 7 for mixtures of methanol-HNO₃ with methanol 99 % and above. The shape of the plots shows that although selectivity is generally satisfactory, a linear function of R_F vs. Z is not followed at such high alcohol concentrations so that selectivity is higher for the elements in the middle of the light lanthanide group.

To investigate the effect of the presence of water in the methanol eluent, some experiments were performed by using acid-free methanol-water mixtures from 100 % to 0 % in alcohol. The results in Fig. 8 show that both adsorption and selectivity only

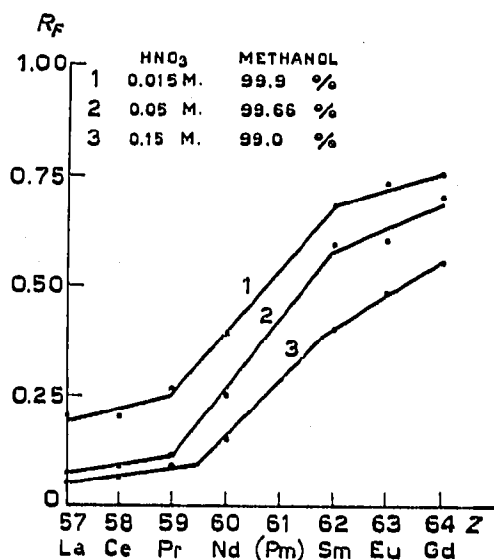


Fig. 7. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with HNO₃-methanol mixtures of composition indicated.

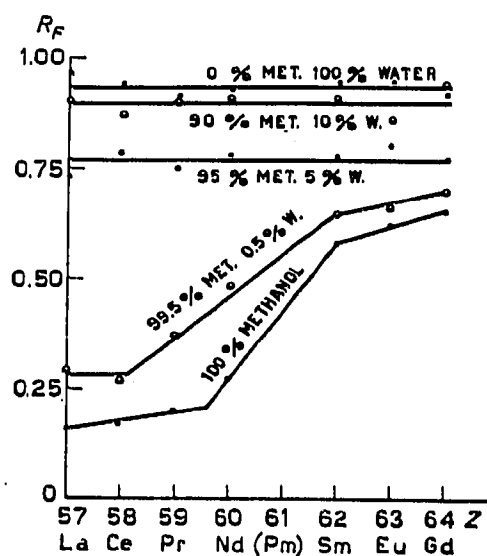


Fig. 8. Plots of R_F vs. atomic number of light rare earths: elution of DE-20 paper with water-methanol mixtures of composition indicated.

become considerable at higher methanol concentration. In fact the plot differs from a horizontal straight line only above 95 % methanol. As already shown in Fig. 7 for high methanol concentrations in HNO₃ the plot is not a straight line but presents a higher selectivity for the elements in the middle of the light lanthanide group. The elution with 100 % methanol gave slightly tailed spots. The similarity between plots of high methanol concentration either with water or with nitric acid suggests that the effect is mainly due to the presence of alcohol provided that the anion-exchange paper is pre-treated to assume the nitrate form (standard procedure), after which paper presents a pH equal to 1. It was also shown that elutions with 99.9 % methanol-water on untreated DE-20 (free hydroxyl base form) gave consistently zero R_F as expected from the pH of paper which is approximately 10, precipitation of hydroxides at the point of application being most likely.

The quantity $1/R_F - 1$ can be considered proportional to the adsorption coefficient and hence the behaviour of DE-20 paper evaluated. The results for two representative rare earths, cerium and samarium, have been collected and plotted in terms of $1/R_F - 1$ against methanol percentage in the alcohol-acid mixture (see Figs. 9 and 10). The increase of adsorption with the increase of both alcohol concentration and

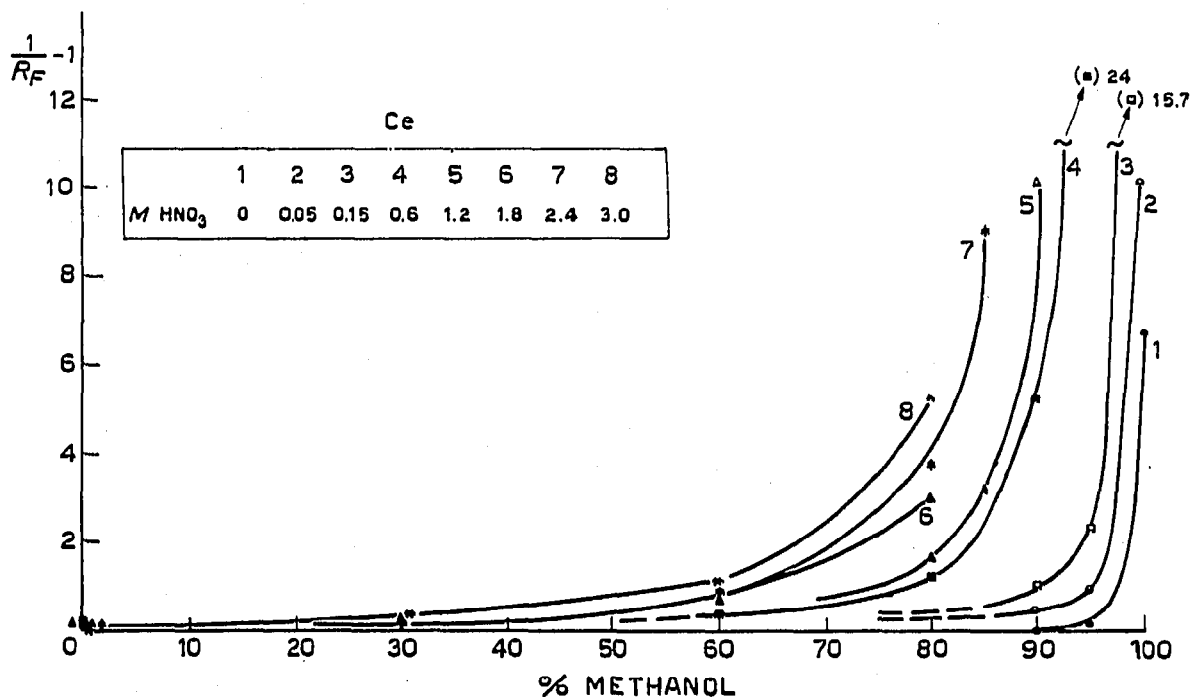


Fig. 9. Effect of methanol percentage (vol.) in the eluent at the quoted HNO₃ molarities on the adsorption of cerium on DE-20 paper.

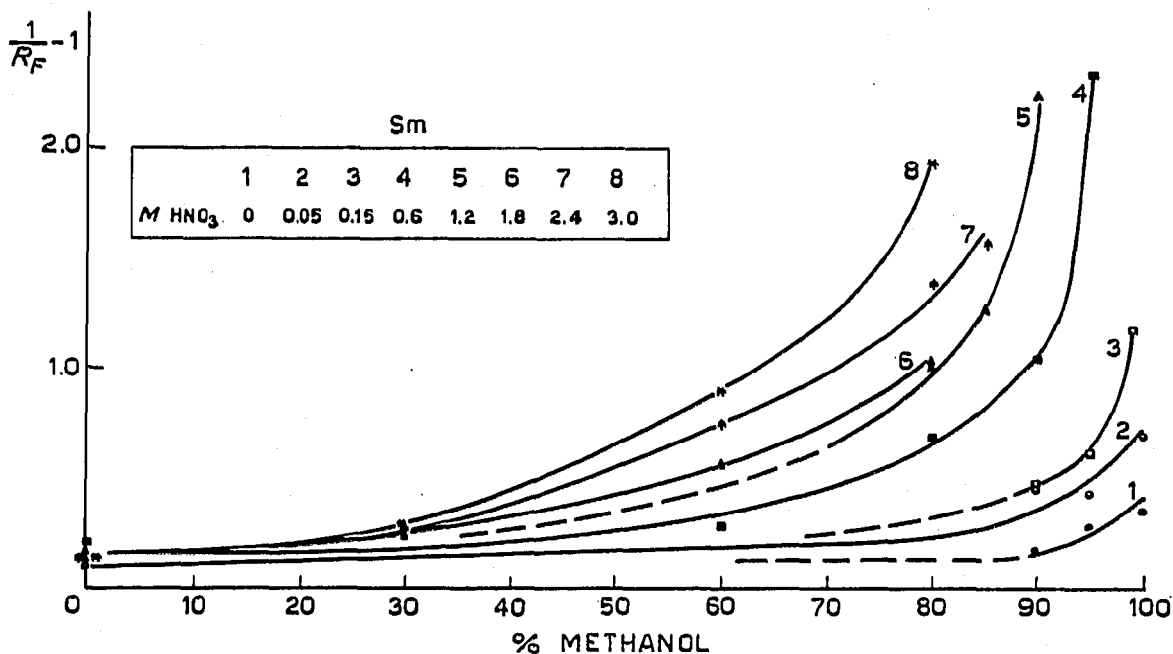


Fig. 10. Effect of methanol percentage (vol.) in the eluent at the quoted HNO₃ molarities on the adsorption of samarium on DE-20 paper.

HNO_3 molarity is clearly apparent. A comparison between the two figures shows that under the same conditions samarium is less adsorbed than cerium as expected from the atomic number, in fact the $1/R_F - 1$ scale for cerium is 5 times greater than that for samarium.

Chromatography on pure cellulose paper

To determine the effect of pure cellulose on the overall phenomenon, a series of experiments were carried out with normal CRL/1 Whatman paper after pre-treatments analogous to those for DE-20 and with the same eluents. As expected, pure cellulose paper showed a lower adsorption of the rare earths than that of the anion-exchange paper, such adsorption being slightly dependent on pre-treatment method. Since no appreciable difference in R_F occurs for the different rare earths on CRL/1, the average R_F values ranged between 0.65 and 0.74 depending on the pre-treatment method. The lower value 0.65 was obtained with the standard pre-treatment procedure already described for DE-20.

A series of experiments were carried out with CRL/1 paper after standard pre-treatment and R_F 's measured as functions of both methanol concentration and HNO_3 molarity. Due to the absence of a significant selectivity within the different rare earths in this case, the average R_F values were considered, although experiments had been carried out with every element of the group cited above. The collected experimental results in Table III show that the behaviour on pure cellulose paper is substantially

TABLE III

AVERAGE R_F VALUES OF LIGHT RARE EARTHS ON CRL/1 CELLULOSE PAPER AS FUNCTIONS OF METHANOL PERCENTAGE AND HNO_3 MOLARITY IN THE ELUENT

$\text{CH}_3\text{OH} \%$	$M \text{HNO}_3$								
	0	0.015	0.05	0.15	0.6	1.2	1.8	2.4	3.0
0	—	—	0.86	—	0.84	0.84	0.84	0.84	0.84
30	—	—	—	—	—	—	0.75	—	0.82
60	—	—	—	—	0.71	—	0.66	0.62	0.64
70	—	—	—	—	0.66	—	0.63	—	—
80	—	—	—	—	0.66	0.53	0.63	0.54	0.59
85	—	—	—	—	0.68	0.60	0.73	0.57	—
90	—	—	0.68	0.60	0.70	0.63	—	—	—
95	0.78	—	0.66	0.68	0.72	—	—	—	—
99	—	—	—	0.67	—	—	—	—	—
99.66	—	—	0.68	—	—	—	—	—	—
99.90	—	0.74	—	—	—	—	—	—	—

different from that on an anion-exchange paper since, as noted before, not only selectivity is negligible but also the effect of HNO_3 molarity on adsorption is very limited. The methanol concentration appears to influence the adsorption to some extent and maximum adsorption (minimum R_F) occurs around 80%.

The effect of temperature on the R_F value

The elution temperature between 0° and 50° was shown to have little effect on the R_F value.

TABLE IV
EFFECT OF TEMPERATURE ON R_F

Rare earth	R_F		
	0°	20°	50°
Cerium	0.62	0.63	0.69
Samarium	0.65	0.66	0.70

Cerium and samarium were eluted with 60% methanol-1.8 M HNO₃ at 0°, 20° and 50°. As shown in Table IV the effect is practically negligible between 0° and 20° and only becomes a little more significant between 20° and 50°.

The separation of rare earths on DE-20 paper

After the experiments referred to above, conditions for the separation of two or more rare earths from a mixture were selected. Elutions were made by ascending chromatography in closed atmosphere at 20° ± 2° with 2 × 20 cm strips. Results, which are in sufficient agreement with predictions from initial experiments are reported in Table V. As an example the diagrams of separations of La-Nd-Sm and La-Sm-Gd are given in Fig. 11.

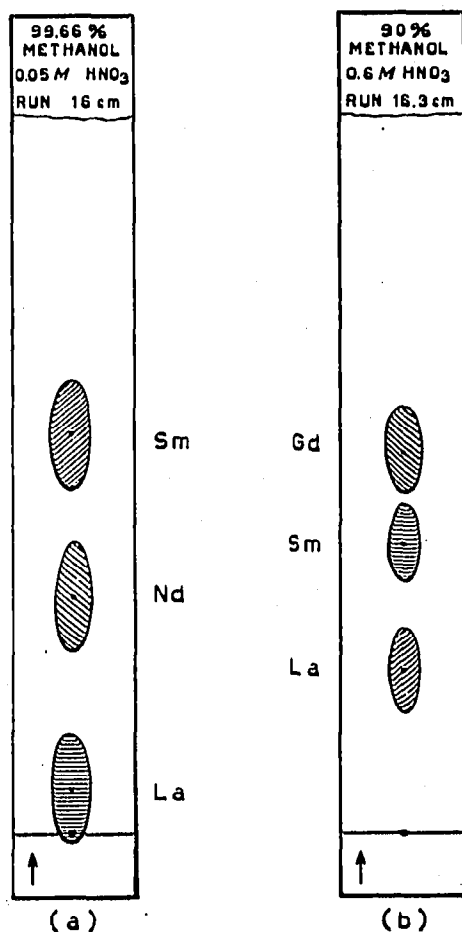


Fig. 11. Diagram of chromatographic separations of Sm-Nd-La (a) and of Gd-Sm-La (b) on DE-20 paper. Ascending elution with eluent indicated in the figure.

TABLE V

SOME ASCENDING CHROMATOGRAMS OBTAINED WITH 2 × 20 cm DE-20 STRIPS UNDER DIFFERENT CONDITIONS

Separations	Run (cm)	Eluent		R_F
		Nominal M HNO_3	% CH_3OH	
Ce-Nd-Gd	14.6	2.4	80	Ce = 0.27; Nd = 0.40; Gd = 0.54
La-Sm-Gd*	16.3	0.6	90	La = 0.23; Sm = 0.40; Gd = 0.53
Ce-Nd-Eu	15.6	1.2	90	Ce = 0.13; Nd = 0.29; Eu = 0.46
Ce-Pr	16.5	0.15	95	Ce = 0.24; Pr = 0.38
Ce-Nd-Sm	17.4	0.15	99	Ce = 0.06; Nd = 0.21; Sm = 0.40
Pr-Sm-Gd	17.2	0.15	99	Pr = 0.12; Sm = 0.46; Gd = 0.60
La-Nd-Sm*	16.0	0.05	99.66	La = 0.06; Nd = 0.33; Sm = 0.56
La-Nd-Gd	15.2	0.15	99.9	La = 0.17; Nd = 0.37; Gd = 0.61
Ce-Nd-Sm	16.0	0.15	99.9	Ce = 0.11; Nd = 0.41; Sm = 0.60

* See Fig. 11.

CONCLUSIONS

The chromatographic separation of rare earths belonging to the La to Gd group on anion-exchange paper (DE-20) has been experimentally shown to be possible when HNO_3 -methanol mixtures are used as eluents.

Other conditions being equal, the R_F value is an increasing function of the atomic number when elution is performed with a mixture containing a high percentage of alcohol. In this case the separative effect is high enough to permit separation of adjacent pairs of lanthanides.

It must be pointed out that, by comparison, much larger separation effects are exhibited by papers treated with the cation exchanger di-(2-ethylhexyl)-orthophosphoric acid (HDEHP) eluted with HCl, as reported in a previous work⁸. Besides the somewhat lower selectivity of the anion-exchange paper with respect to the liquid cation-exchange-treated paper, it must be pointed out that the latter paper can be applied to the whole lanthanide group whereas the DE-20 paper eluted with HNO_3 -methanol mixtures is effective with the light rare earth group only. As for the general aspects, whilst with the anion-exchange paper the adsorption decreases with atomic number, with the HDEHP-treated paper it increases with atomic number.

The anion-exchange paper adsorbs each rare earth more strongly the higher the methanol concentration. Such an effect was also found by LEDERER *et al.*⁹ in the elution of several elements, among them lanthanum on a quaternary ammonium resin loaded paper (Amberlite SB-2) with HNO_3 -ethanol mixtures.

In spite of the considerable experimental evidence that in this case both adsorption and selectivity depend upon the presence of diethylaminoethyl-cellulose groups on the paper, since pure cellulose paper behaves in a totally different way, such phenomena cannot be completely attributed to an anion-exchange process. In fact experiments performed under the same conditions of HNO_3 molarity and methanol content with liquid-liquid extraction with the liquid anionic exchanger tri-*n*-octylamine, gave no evidence of any adsorption of the element into the organic phase, whereas it occurs with solid anion-exchange resins⁸.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the collaboration of Mr. ANTONIO ALBINI in the laboratory work.

SUMMARY

The chromatographic behaviour of rare earths from La to Gd has been investigated in HNO₃-methanol systems on the anion-exchange paper DE-20. The possibility of separation of two or more rare earths from each other has been shown as a consequence of the favourable effect of high methanol concentrations on selectivity. A comparison was also made with results obtained by elution under the same conditions on pure cellulose CRL/I paper. This paper possessed only limited adsorption properties and did not show any selectivity toward different rare earths.

The fact that in the liquid-liquid extraction system with the liquid anion exchanger tri-*n*-octylamine no rare earth adsorption occurs into the organic phase suggests that the adsorption and selectivity shown by the anion-exchange paper is not attributable to a pure anion-exchange process.

REFERENCES

- ¹ D. H. WILKINS AND G. E. SMITH, *Talanta*, 8 (1961) 138.
- ² J. S. FRITZ AND D. J. PIETRZYK, *Talanta*, 8 (1961) 143.
- ³ J. KORKISCH, I. HAZAN AND G. ARRHENIUS, *Talanta*, 10 (1963) 865.
- ⁴ J. P. FARIS AND J. W. WARTON, *Anal. Chem.*, 34 (1962) 1077.
- ⁵ C. TESTA, *Anal. Chem.*, 34 (1962) 1556.
- ⁶ M. LEDERER AND V. MOSCATELLI, *J. Chromatog.*, 13 (1964) 194.
- ⁷ R. ARNOLD AND J. F. RITCHIE, *J. Chromatog.*, 10 (1963) 205.
- ⁸ E. CERRAI AND C. TESTA, *J. Chromatog.*, 8 (1962) 232.
- ⁹ M. LEDERER, V. MOSCATELLI AND C. PADIGLIONE, *J. Chromatog.*, 10 (1963) 82.

J. Chromatog., 16 (1964) 365-375