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RARE EARTH SEPARATIONS USING CATION-EXCHANGE COLUMN CHROMATOGRAPHY

COMPARISON OF α-HYDROXYISOBUTYRIC ACID AND α-HYDROXY-α-METHYLBUTYRIC ACID AS ELUANTS

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SUMMARY

Separations of several adjacent rare earth pairs were investigated in order to compare the effectiveness of two eluting agents: α-hydroxyisobutyric acid (αHIBA) and α-hydroxy-α-methylbutyric acid (αHαMBA). The latter was found to be superior for certain rare earth pairs.

INTRODUCTION

Rare earth separations using cation-exchange column chromatography have been successfully achieved using a variety of complex-forming reagents as eluants. In particular, α-hydroxycarboxylic acids such as α-hydroxyisobutyric acid (αHIBA), citrate, glycollate and lactate or aminopolyacetic acids such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) all as the ammonium salts are used to elute trivalent lanthanides sequentially from strong-acid cation-exchange resins such as Dowex 50W or Zeocarb 225[1]. The ammonium salt of α-hydroxyisobutyric acid (αHIBA) has been regarded as providing the greatest degree of separability between adjacent lanthanides (and actinides) in ion-exchange chromatography (although still better separations may be achieved for certain rare earths by resorting to reversed-phase partition chromatography using organophosphorus compounds as chelating agents[2,3]). In 1964, NISHI AND FUJIWARA[4] reported that α-hydroxy-α-methylbutyric acid (αHαMBA) provided better chromatographic fractionation than αHIBA for the rare earth elements. In particular, the average separation factor for adjacent rare earths using αHαMBA was 1.77 compared to the equivalent average of 1.60 for αHIBA as determined from the work of CHOPPIN AND SILVA[5]. Improved separations with αHαMBA were evident, however, only for a few specific adjacent rare earth pairs. Since extent of fractionation as measured through separation factors can vary considerably from laboratory to laboratory as the particular reagents, apparatus and conditions are not of necessity identical, it is necessary to compare the chromatographic effectiveness of αHIBA and αHαMBA towards rare earths under identical operating conditions.

MATERIALS AND METHODS

Apparatus

A single chromatographic column 30.0 × 0.28 cm of borosilicate glass obtained from Chromatronix, Inc. (Berkeley, Calif., U.S.A.) was used for all elution experiments. The column was filled with Bio-Rad AG 50 X12, 400 mesh resin (Bio-Rad Laboratories, Richmond, Calif., U.S.A.) from which the fines had been removed and which had previously been converted to the NH_4^+ form by batch titration with NH_4OH. The eluant was fed at controlled flow-rate by a Milroy pump (Milton Roy Co., St. Petersburg, Fla., U.S.A.) through a sample injection valve (Chromatronix, Inc.) on to the column as shown in Fig. 1. An LKB (Stockholm, Sweden) UltroRac 7000 fraction collector was used to accumulate elution samples. A NaI(Tl) scintillation well-detector assembly served to assay the gross gamma-radioactivity in each fraction.

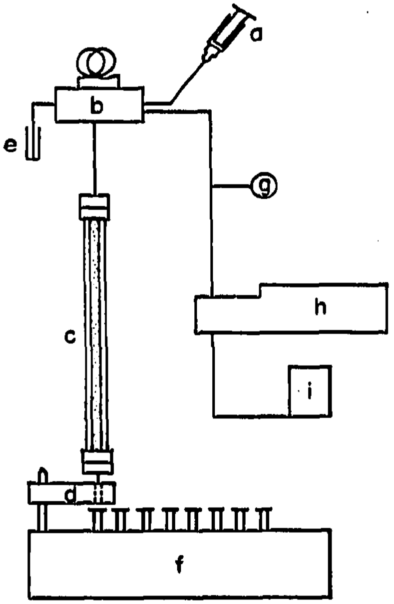

Fig. 1. Chromatography apparatus. Components: a, syringe; b, sample injection valve with sample loop; c, column; d, drop counter; e, sample vessel; f, fraction collector; g, pressure gauge; h, eluant delivery pump; i, eluant reservoir.

Reagents

Appropriate quantities of αHIBA and αHαMBA, both obtained from K & K Laboratories, Inc. (Plainview, N. Y., U.S.A.), were dissolved in distilled water, made *ca.* 0.05 % in formaldehyde (acting as fungicide), and both titrated to pH 4.0 using concentrated NH_4OH, providing 0.25 F solutions. As radioactive tracers, carrier-free ^{145}Pm, ^{145}Sm, ^{147}Nd, ^{154}Eu, ^{169}Yb and ^{170}Tm obtained from New England Nuclear (Boston, Mass., U.S.A.) and C.E.A. (Gif-sur-Yvette, France) were prepared as 0.05 *N* HCl solutions. Reagent grade ammonium citrate was used to prepare 5 % ammonium citrate solution.

Procedure

All experiments were conducted at room temperature. Eluant was pumped through the column until constant pH of the effluent was attained, serving as evidence for equilibrium conditions on the resin. Eluant flow continued at the desired flow-rate while the tracer mixture was loaded into the sample loop of the sample injection valve. Fraction collection was commenced simultaneously with the injection of the sample into the flow system. One-ml fractions were collected and assayed. Subsequent to the completion of sample elution, approximately 20 ml of 5 % ammonium citrate was pumped through the system followed by *ca.* 30 ml of water to remove any undesirable cations such as residual lanthanides or alkaline earth impurities. The column was next re-equilibrated with the appropriate eluting agent and the chromatographic process repeated. In this manner, the conditions were maintained identical from elution to elution regardless of which eluting reagent was in use.

The resin column height measured 29.0 cm under operating conditions during which the flow-rate was 3.0 ± 0.2 min/ml. Column void volume amounted to 1.5 ml which included the dead volume in the sample delivery system between the sample injection point and the top of the resin bed.

RESULTS AND DISCUSSION

The standard method for expressing relative separation of various species eluted from chromatographic columns is through the separation factor. The separation factor α_A^B for substances A and B is given by

$$\alpha_A^B = (V_B - V_0)/(V_A - V_0)$$

where V_A and V_B are the volumes at which the elution peaks occur for A and B respectively. V_0 represents the system void volume, 1.5 ml in this case. A typical

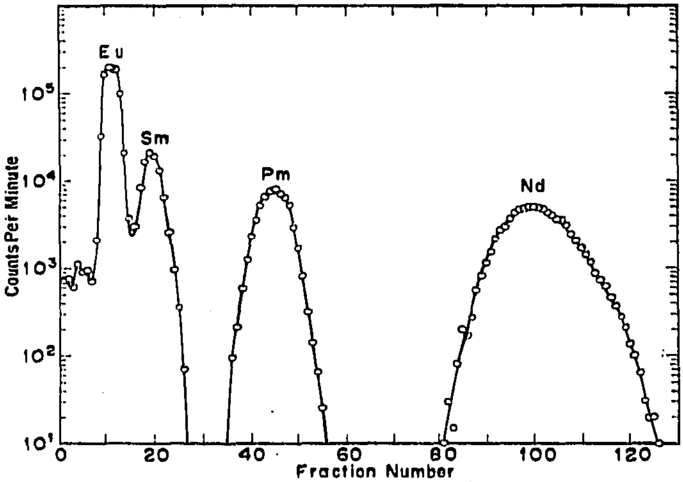

Fig. 2. Elution curve for Eu, Sm, Pm and Nd. Column, 29.0 × 0.28 cm; resin, Bio-Rad AG 50X 12, 400 mesh, NH_4^+ form; flow-rate, 5.4 ml·cm^{-2}·min^{-1}; eluant, 0.25 F αHαMBA pH 4.0 ambient temperature.

TABLE I

SEPARATION FACTORS FOR ADJACENT RARE-EARTH PAIRS

Figures in parentheses following separation factors represent the number of duplicate determinations.

	Tm–Yb	*Sm–Eu*	*Pm–Sm*	*Nd–Pm*	*Reference*
αHIBA (25°)[a]	1.55(2)[b]	1.81(5)	2.05(6)	1.73(5)	this work
αHαMBA (25°)[a]	1.50(2)[b]	1.83(2)	2.44(2)	2.31(2)	this work
αHIBA (25°)[c]	1.38	2.1	1.6	2.1	6
αHIBA (87°)[d]	1.33	1.60	1.82	1.61	5
αHIBA (87°)[e]	—	2.0	1.83	1.82	7
αHαMBA (87°)[d]	1.35	1.98	1.75	1.48	4

[a] Bio-Rad AG 50 X12 resin.
[b] Bio-Rad AG 50 X12 resin, 0.10 F αHIBA and αHαMBA pH 3.8.
[c] Dowex 50 X4 resin.
[d] Dowex 50 X8 resin.
[e] Dowex 50 X12 resin.

TABLE II

OPERATING CONDITIONS FOR COLUMN SEPARATIONS USING αHαMBA

Item	*Ref. 4*	*This work*
Column size	32.0 × 2.0 cm	29.0 × 0.28 cm
Resin	Dowex 50 X8, 100–200 mesh	Bio-Rad AG 50 X12, 400 mesh
Operating temperature	87°	25°
Flow-rate	2.5–3.0 ml·cm^{-2}·min^{-1}	5.4 ml·cm^{-2}·min^{-1}
[αHαMBA]	0.20 F	0.25 F

elution curve from this work is shown in Fig. 2. Table I compares the separation factors for the adjacent rare earth pairs studied in this work. Uncertainties associated with these separation factors (first two rows) are estimated to be less than 2.5 % as determined from data analysis and reproducibility.

Unlike reported in ref. 4, the difficulties associated with comparing separation effectiveness of different eluting agents performed under different circumstances have been eliminated in this study. The data in Table I show that αHαMBA is indeed more effective than αHIBA in resolving certain mixtures of rare earth elements by ion-exchange chromatography. It should also be noted that the separation factors reported in this work differ from those of NISHI AND FUJIWARA[4], being generally of greater magnitude, a result attributable to the differences in operating conditions, summarized in Table II, between the two laboratories. As can be inferred from the various αHIBA results in Table I, no general correlation between the value of any particular separation factor and column operating conditions (temperature, resin cross linkage, flow-rate) is evident, but rather must be individually determined. Indeed, the apparent sensitivity of separation factors to column characteristics can obscure differences between various eluting reagents. This is especially evident for the Nd–Pm separation where the results of NISHI AND FUJIWARA suggested αHαMBA to be less effective than αHIBA by 14 % compared to an improvement of 34 % demonstrated in this investigation.

The conclusion that αHαMBA is a more effective separating agent for rare earth elution chromatography should, following the above discussion, be applied with care when contemplating rare earth pairs other than those considered in this investigation. Further work is in progress to help clarify this point.

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