RARE EARTH CHROMATOGRAPHY USING
BIS-(2-ETHYLHEXYL) ORTHOPHOSPHORIC ACID

JOHN W. WINCHESTER

*Department of Geology and Geophysics, M.I.T.,
Cambridge, Mass. (U.S.A.)*

Bis-(2-ethylhexyl) orthophosphoric acid*, DEP, has been found by PEPPARD et al.[1], to form very selective complexes with the trivalent lanthanide and actinide ions. DEP, $(CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH_2O)_2PO(OH)$, a monobasic acid insoluble in dilute acidic aqueous solutions, has been used in solvent extraction of the rare earths. In its pure form the separation factors for adjacent rare earths are uniformly close to 2.5, and the higher atomic number lanthanides are the more tightly complexed.

SIERKIERSKI AND FIDELIS[2,3] have carried out chromatographic separation of the rare earths using tributyl phosphate held on a column of diatomaceous silica, first made hydrophobic with dichlorodimethylsilane vapors. In their system elution was carried out with nitric acid.

In this work the rare earths are separated chromatographically using columns of DEP held on dichlorodimethylsilane-treated diatomaceous silica columns. Separation factors observed are similar to those in solvent extraction using DEP, and the kinetics of the elution are rapid. Columns are easily prepared and are stable and long-lived. Similar results were obtained independently by CERRAI et al.[4] using columns of cellulose.

EXPERIMENTAL

Column substrate material is Johns-Manville Celite Analytical Filter Aid, used directly as supplied by the manufacturer. The surface is made hydrophobic by placing several grams of Celite in a desiccator containing an open bottle of dichlorodimethylsilane, allowing about two days of contact time, and heating briefly and washing with methanol to remove hydrogen chloride released during the reaction. The dried product is slurried with an acetone solution of DEP such that the weight ratio of DEP to Celite is about 1:5. After a few minutes the acetone is evaporated with gentle heating until the odor of acetone is gone. The dry-looking product is then slurried with 0.01 N HCl containing a wetting agent (0.1 % of the polyester Tergitol Nonionic NPX, manufactured by the Union Carbide Co., Inc., is satisfactory) and held at 90° for two days until all particles settle out easily and no air bubbles remain. Removal of air bubbles is critical for subsequent column operation.

A column is packed by allowing the slurry to settle out in a suitable glass tube. Elution using columns of the dimensions reported in this paper requires a few pounds

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* Also known as di-(2-ethylhexyl) orthophosphoric acid and di-(2-ethylhexyl) hydrogen phosphate and abbreviated HDEHP and D2EPA.

per square inch (several tenths of an atmosphere) of external pressure. If the column is properly packed and free of air bubbles, the bed should not be visibly compressed upon application of the pressure.

PEPPARD et al.[1] have stressed the necessity for purity of the DEP reagent in achieving the maximum separation factors, particularly for La and Ce. Small amounts of the dibasic acid, mono-(2-ethylhexyl) orthophosphoric acid, form strong and rather unselective complexes with the trivalent lanthanides. PEPPARD et al.[1] describe a solvent extraction procedure for purification of impure material. For this work, however, specially prepared DEP of high purity obtained from the Oak Ridge National Laboratory was used.

Loading the column is most easily carried out by treating the column with solution of the same acidity as that of the sample and allowing the sample in a small volume ($\sim$ 2 ml for columns reported here) to soak into the top of the bed. Pressure may be used in this operation, but care must be exercised not to allow any air to be forced into the column. The acidity of the solution during the loading operation must be such that the sample is strongly adsorbed. For rare earths in this work, 0.05 N HCl or HNO_3 is satisfactory. For efficient uptake of the rare earths by the column, the solution must be quite free of all other cations of charge 2 + and greater.

The heating jacket for columns used at elevated temperature consists of a 3 cm glass tubing surrounding the column and secured by rubber stoppers at the ends such that warm water can be passed into the bottom and out the top. The warm water line is heated by a constant temperature bath to about 70°. All eluent solutions are outgassed by heating on a steam bath prior to use. If air bubbles are inadvertently formed in the column, they can be resorbed by eluting with outgassed solution.

RESULTS

Rare earths in the presence of a large excess of DEP react to form complexes which may be described by equilibria of the type:

$$M^{3+} + 3HL = ML_3 + 3H^+$$
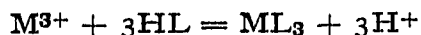
where HL represents the free acid and L^- the anion. Actually molecular weight determinations by BAES et al.[5] indicate that the complex contains 6 moles of DEP per mole of rare earth, but in dilute solutions the dependence of the equilibrium on acidity and reagent concentration is nevertheless accurately given by the above equation. Therefore, we may write an expression for an equilibrium constant

$$K = \frac{(ML_3)\,(H^+)^3}{(M^{3+})\,(HL)^3}$$

In a solvent extraction system the free reagent and the complex are present primarily in the organic phase, and the rare earth and hydrogen ions are concentrated in the aqueous phase. This expression therefore describes the ratio of rare earth concentrations in the two phases in terms of the acidity of the aqueous phase and the reagent concentration in the organic. Rewriting, the extraction coefficient,

$$E_a{}^o = \frac{(ML_3)}{(M^{3+})} = K\,\frac{(HL)^3}{(H^+)^3}$$

indicates that extraction is repressed by high acidity in the aqueous phase and enhanced by high reagent concentration in the organic. The equilibrium constant K is a characterisitic of each rare earth and increases rather regularly by a factor of 2.5 for each unit of atomic number, according to the extraction studies of PEPPARD et al.[1]. This discussion seems to apply to the organic phase composed of either the pure reagent or the reagent diluted with an inert solvent such as xylene and to either column operation or batch solvent extraction.

In two experiments designed to test column characteristics at room temperature, mixtures of carrier-free [141]Ce + [144]Ce, [143]Pr, [147]Pm and [91]Y radiotracers (obtained from the Isotopes Division, Oak Ridge National Laboratory) were loaded onto columns essentially as described under EXPERIMENTAL. In one of these experiments
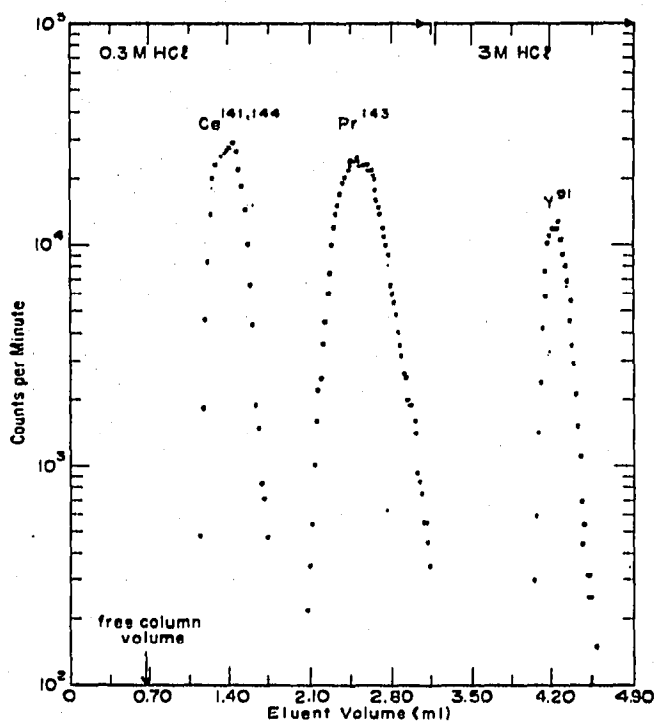

Fig. 1. Elution curve of carrier-free rare earth tracers. Column specifications: Celite + DEP (10:1). 3 cm × 0.24 cm² column, ∼ 70 % void space. Flow rate, 0.037 ml/min or 0.154 cm/min.
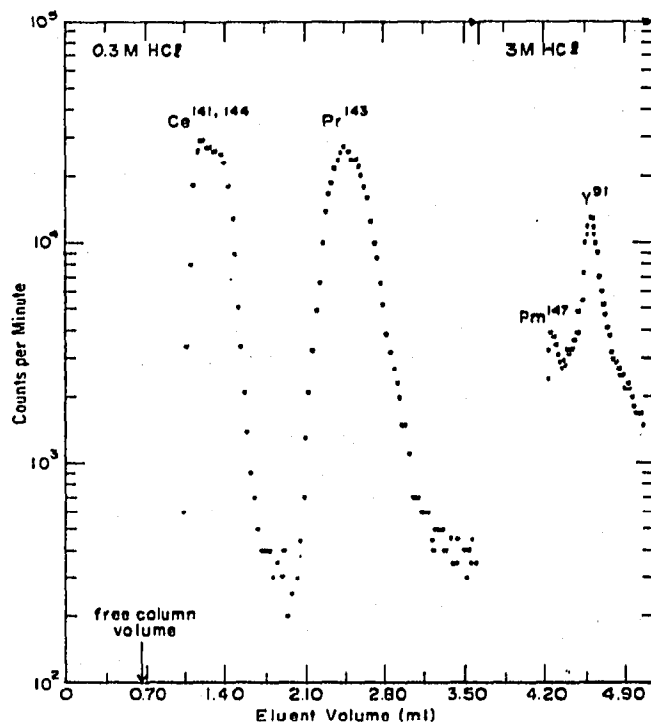
Fig. 2. Elution curve of rare earth tracers + 0.05 μmoles each of Ce, Pr, and Y, equivalent to about 1 % of the column capacity. Elution conditions same as Fig. 1.

the tracers were used in the carrier-free form and in the other they were diluted with 0.05 micromoles each of Ce, Pr and Y, an amount of total rare earth which represented theoretical saturation of about 1 % of the total column capacity. Elution was carried out with 0.3 N HCl until the Ce and Pr were completely removed from the column, and the acid concentration was changed to 3 N. (In the elution of the carrier-free tracer mixture, an intermediate elution with 0.5 N HCl was also included to remove the [147]Pm separately.) Elution was carried out slowly, the whole process requiring two hours, and the resulting elution curves, obtained by beta counting single drops collected and dried on a moving paper strip, are shown in Figs. 1 and 2. The separation of Ce from Pr is better for the carrier-free tracers, having a peak to valley ratio of the order of 10^3, but the separation of the tracers with added carriers gives a peak to
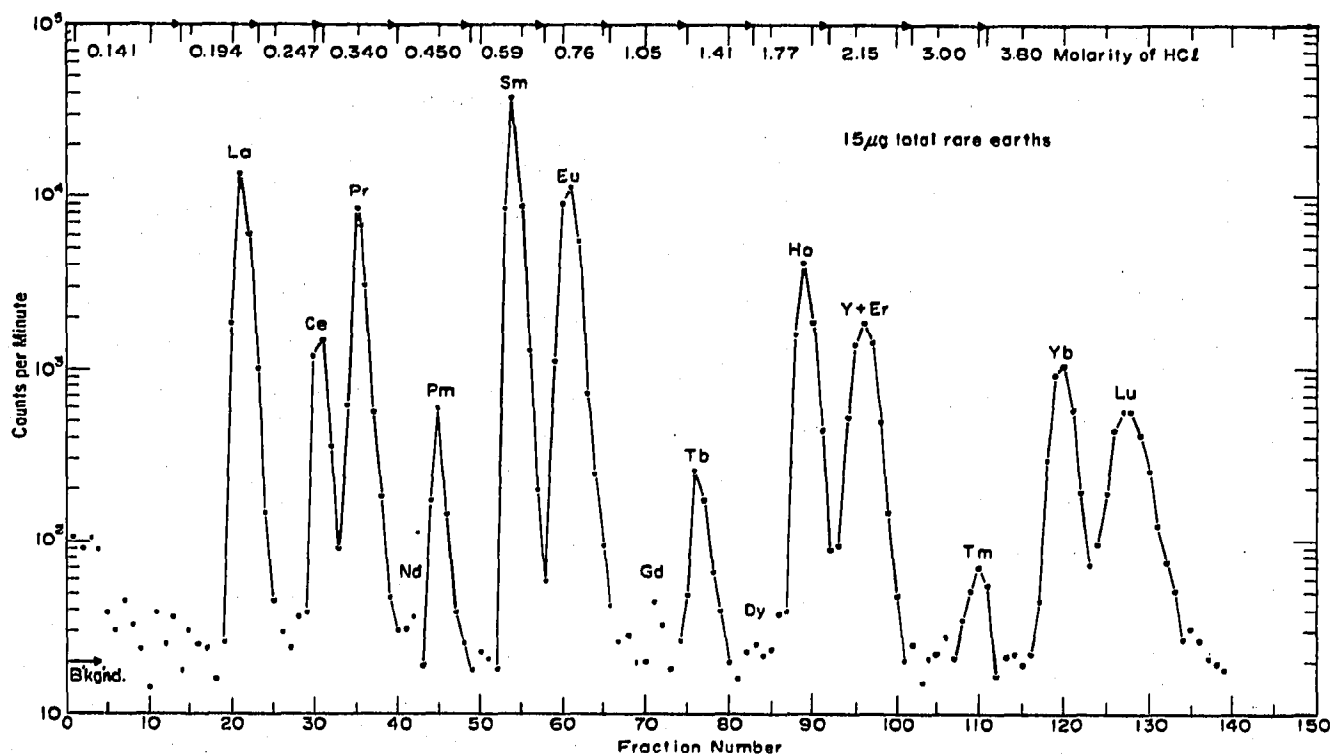
Fig. 3. Typical elution curve for rare earth separation. RE totalling 15 μg, in relative amounts as they occur in average shale (80% Ce, Y, Nd, and La), were dissolved in 1 ml 0.05 N HNO_3, irradiated 1 h at 10^{13} n/cm^2 sec, and eluted 19–23 h later. Ten-drop fractions were evaporated and β-counted for 1 min each 38–41 h after irradiation. The column was 6 cm long and contained 1.9 ml total volume. Elution was carried out at 60–$70°$, 10 drops per fraction, and 1 fraction per minute. (Elution by 6 ml of 0.05 N HNO_3 preceded the HCl to remove traces of ^{24}Na and other radioactivities.)

valley ratio of about 10^2. It is interesting to note that the position of the peaks depends somewhat on the amount of rare earth present under high loading conditions.

In applying the procedure to separating the entire series of rare earths, a stepwise gradient of hydrochloric acid concentration was selected such that each concentration, if used alone, would bring one of the rare earths off the column in about two free column volumes, where the free column volume is about 70% of the geometrical volume of the column bed. An elution curve at $70°$ for a mixture of rare earths, corresponding roughly to their abundance in 0.1 g of sedimentary rock and irradiated with pile neutrons for an hour, is shown in Fig. 3. The acid concentrations used in the gradient steps are indicated at the top of the figure. It appears that separations are regularly sharp along the series sufficient for graphical resolution and peak integration to an accuracy of several per cent in most cases.

Application of the DEP rare earth chromatographic procedure to neutron activation analysis in geochemistry is now in progress.

ACKNOWLEDGEMENTS

SUMMARY

Sharp separations of microgram amounts of the lanthanide elements as trivalent ions in aqueous hydrochloric acid solution are made chromatographically using a column of diatomaceous silica made hydrophobic with dichlorodimethylsilane vapors and coated with high purity bis-(2-ethylhexyl) orthophosphoric acid (DEP). Separation factors averaging 2.5 for adjacent rare earths are observed, as in solvent extraction using DEP, such that the higher atomic number elements are more tightly held by the column. The kinetics of the sorption–desorption process appear to be very fast, but elutions at 70° appear to be somewhat sharper than at 25°, especially at high flow rates and high loading. A heated column 5 cm long and 2 cm³ total volume (70 % void space) has been used to separate 15 micrograms of mixed lanthanides from each other in 3 h using a stepwise gradient from 0.14 to 3.8 N HCl. La is eluted first, and Y is eluted together with Er.

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