

Use of Di-(2-ethylhexyl) Orthophosphoric Acid for the Separation of the Elements Lanthanum-Gadolinium by Reverse Phase Partition Chromatography

INVESTIGATIONS into the use of alkyl phosphoric acids as metal extractants have shown that there are relatively large differences between the stabilities of the complexes of individual rare earths with di-(2-ethylhexyl) orthophosphoric acid (HDEHP), the separation factor for any adjacent pair being about 2.5¹. This figure suggests that it should be feasible to devise a comparatively simple scheme for rare earth separations based on a multi-stage extraction procedure utilizing HDEHP as extractant. If the organic reagent can be immobilized on a solid phase the effect of a number of successive extractions may be achieved by eluting the metals chromatographically from a column of the extractant, and it has already been shown that complexing agents may be incorporated into solid supports to provide column materials of this type²⁻⁶. Investigations into the behaviour of a number of support materials retaining HDEHP have indicated that a poly-(vinyl chloride/vinyl acetate) copolymer ('Corvic', Imperial Chemical Industries, Ltd.) will hold the complexing agent firmly and will give elution curves with the rare earths which show relatively little tailing. Using columns packed with 'Corvic' retaining HDEHP it has been found possible to separate small quantities of the elements lanthanum-cerium-praseodymium-neodymium-promethium-samarium-europium and gadolinium, using normal chromatographic techniques.

Column material was made up by mixing the poly-(vinyl chloride/vinyl acetate) copolymer with a solution of chloroform (5 ml.), toluene (3 ml.) and purified HDEHP¹ (2 ml.) in the ratio of 10 gm. of solid to 10 ml. of solution. Organic solvent was evaporated off until the total weight of 10 gm. dry weight of 'Corvic' plus the adsorbed liquid was 12.5-12.7 gm., when the resulting powder was first slurried in *N*/500 perchloric acid, then made up into a column of the required size in the usual way. The temperature of the column was thermostatically controlled at 60° C., column size was 1 cm. diameter × 30 cm. and the flow-rate was approximately 1.0 ml./cm.²/min. Between 0.01 and 0.1 mgm. of the irradiated trivalent elements lanthanum-gadolinium (with the exception of promethium) were added to the top of the column, as required, in very dilute acid solution, and the column then washed with *N*/500 perchloric acid. In the initial experiments, when the behaviour of adjacent pairs of rare earths was being considered, the extracted rare earths were eluted with perchloric acid solution of constant strength, but for later experiments, when a more comprehensive separation was required, the acidity of the influent was gradually increased. For the determination of the activity in the column effluent the perchloric acid solution leaving the bottom of the column was either passed through a γ -scintillation flow counter connected to ratemeter and chart recorder, or collected in fractions of 1 ml. or less, and the activity of each fraction assayed separately. The nuclides giving rise to the measured radiation were characterized by γ -ray spectrometry or from half-life curves.

The effectiveness of HDEHP retained on 'Corvic' for the separation of the elements lanthanum-gadolinium may be gauged from Fig. 1, in which the elution of the metals, as recorded by the flow counter, is shown, together with the acidities at peak maxima.

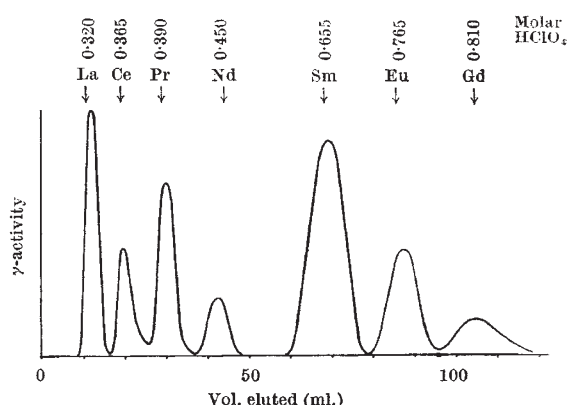


Fig. 1. Separation of the elements La-Gd by gradient elution from a 'Corvic'-HDEHP column

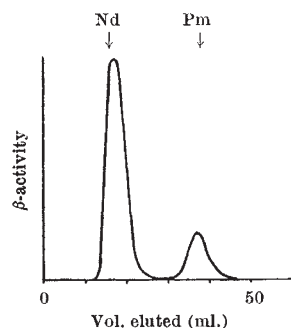


Fig. 2. The elution of Nd and Pm from a 'Corvic'-HDEHP column by 0.39 *M* perchloric acid

The γ -counter used was not sensitive to the largely β -active promethium, but the separation of promethium from neodymium is shown in Fig. 2. It can be seen that a good resolution of the elements is achieved by a simple gradient elution technique which relies only on the differences in the stabilities of the individual metals with HDEHP, and does not require the addition of complexing anions to the eluting phase.

The separation of cerium from praseodymium and europium from gadolinium proved troublesome when perchloric acid of constant acidity was employed as influent to the column, but gradient elution greatly reduced overlap of the elements in the effluent, and permitted a separation to be achieved, even for the europium-gadolinium pair, which has been previously shown to be difficult to isolate by different techniques^{2,7}.

We thank Mr. J. R. Fryer for valuable help given in the initial stages of this work.

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