Use of Di-(2-ethylhexyl) Orthophosphoric Acid for the Separation of the Rare Earths by Reverse Phase Partition Chromatography

It has been shown that relatively large separation factors may be obtained for adjacent rare earths by liquid-liquid extraction if di-(2-ethylhexyl) orthophosphoric acid (HDEHP) is used as the organic extractant¹. In an earlier communication² we have considered the possibility of exploiting the properties of HDEHP for separating the elements from lanthanum to gadolinium by reverse phase partition chromatography, the HDEHP being retained on a solid support, packed to form a chromatographic column. It was found that the elements were removed from dilute perchloric acid to form a band at the top of the column, and then could be eluted successively in the order of increasing atomic number by means of perchloric acid of gradually increasing strength, good resolution of the individual rare earths being obtained. Further investigations have now shown that this technique may be extended to provide a separation of the heavy rare earths terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, gradient elution again being used to provide column influents of the wide range of acidities necessary for the elution of these elements.

A column material of purified HDEHP¹ retained on the 100-150 mesh fraction of a poly(vinyl chloride/vinyl acetate) copolymer ('Corvic', Imperial Chemical Industries, Ltd.) was made up as before² and this was then slurried and packed to form a column 1 cm. diam. $\times$ 60 cm. long which was maintained at a temperature of 60°C. by a thermostatically controlled water jacket. Solutions containing 0.05-0.5 mgm. of the irradiated trivalent lanthanides were added to the top of the column in dilute perchloric acid, and the elements were then eluted with perchloric acid of gradually increasing strength at a flow-rate of approximately 2.0 ml./cm.²/min. The behaviour of promethium was determined by assay of the γ -activity of the 27-hr. promethium-151 nuclide, which was derived from the parent neodymium-151 produced by an (n,γ) reaction on natural neodymium. The effluent leaving the column was passed first through a γ -scintillation flow counter connected to a rate-meter and chart recorder, and then collected in fractions of 0.5 ml. or less by means of a drop counter operating in conjunction with an automatic fraction collector. The γ -activity of each elution peak was identified by γ -spectroscopy and the acidity of the effluent at the peak maxima determined by titration with standard alkali.

Fig. 1. Separation of the rare earths by gradient elution from a 'Corvic'-HDEHP column

The effect of altering such variables as flow-rate, temperature and HDEHP loading of the columns will be discussed in detail elsewhere, but the separation of the elements lanthanum-lutetium shown in Fig. 1 is typical of that achieved by gradient elution of the rare earths from an HDEHP-'Corvic' column with perchloric acid without adding additional complexing agents to the aqueous phase. Acidities at peak maxima are also quoted.

It can be seen that the elements terbium-lutetium, like the light rare earths, are eluted in the order of increasing atomic number, which is also the order of increasing distribution ratio for the lanthanides, when partitioning between aqueous hydrochloric acid and a solution of HDEHP in toluene, at constant acidity and HDEHP concentration¹. The adjacent rare earths cerium-praseodymium-neodymium, europium-gadolinium, dysprosium-holmium and ytterbium-lutetium proved somewhat difficult to separate, but good resolution was obtained when these elements were eluted from the column with a slowly changing acid gradient, under the conditions of temperature, flow-rate, column loading, etc., used in these investigations.

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¹ Peppard, D. F., Mason, G. W., Maier, J. L., and Driscoll, W. J., *J. Inorg. and Nucl. Chem.*, **4**, 334 (1957).

² Pierce, T. B., and Peck, P. F., *Nature*, **194**, 84 (1962).

BIOCHEMISTRY

Effect of Pyruvate and Acetoacetate on the Metabolism of Fatty Acids by the Perfused Rat Heart

CARDIAC muscle demonstrates great flexibility in the choice of substrates for energy production under various conditions. By coronary sinus catheterization of the intact heart in dogs¹ and man^{2,3}, it has been shown that under conditions of fasting or diabetes mellitus, the heart's principal sources of fuel are fatty acids derived from the non-esterified fraction of plasma, whereas after a carbohydrate-rich meal, glucose, pyruvate, and lactate are the preferred sources of energy. Under these latter conditions of rising concentrations of glucose and the three-carbon acids, the extraction of non-esterified fatty acids by the heart may drop to nil.

In order to explore certain aspects of this metabolic competition *in vitro*, the isolated perfused rat heart preparation described by Bleehen and Fisher⁴ was chosen. The metabolism of palmitate-1-¹⁴C complex by bovine serum albumin⁵ was studied in the presence and absence of 0.01 M sodium pyruvate and 0.01 M acetoacetate, substrates known to be well oxidized by preparations of heart muscle. Bovine serum albumin containing 0.51 mole endogenous fatty acid and 0.30 mole of added palmitate-1-¹⁴C per mole of albumin was made to a concentration of 2 per cent in Krebs-Henseleit bicarbonate medium⁶. Male albino rats 210-280 g in weight fed an adequate stock diet were anaesthetized with diethyl ether, in-