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NOTE

An Improved Ion-Exchange Procedure for the Preparation of High-Purity Yttrium

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Developments in luminescent materials for color television, lighting, and laser materials have created a demand for high-purity rare earths. In these applications it is desired to optimize the unique properties of a specific rare-earth element. This task is made difficult, however, by the occurrence of other rare-earth elements at trace levels and higher. Furthermore, the separation of rare earths by standard chemical methods is difficult because of their similar chemical properties. Ion-exchange chromatography has been applied to this problem of separation, and a great deal of data and information have been reported in the literature (*1*,*2*). Since our main interest was in high-purity yttrium oxide, a complexing agent more suited for yttrium separation was sought.

Asher et al. (*3*) have outlined a scheme using DTPA (diethylenetriaminepentaacetic acid) as the complexing agent for purifying yttrium. Although this method is capable of producing 99.98% pure yttrium oxide, the slight contamination (approximately 200 ppm) of rare earths in yttrium made it unsuitable for the research programs being conducted at the laboratory. An improved method is described using a more efficient ion-exchange resin with electrically heated columns which allows for more uniform heating and improved separation. Yttrium oxide of 99.9999% purity was produced.

EXPERIMENTAL PROCEDURE

Columns

Modified heating tubes, model No. 9340, obtained from Corning Glass Works, were used as the ion-exchange columns. These were 83–120 cm long and 3–6 cm in diameter and were temperature-controlled with a powerstat power supply. Preheaters consisting of glass reservoirs wrapped with heating tape were mounted on top of the columns by means of ground-glass joints. Glass-fitted disks supported the resin.

Resins

Dowex 50W cation exchange resin, in the hydrogen form, was employed. Resins differing in particle size and degree of cross-linking were used and compared for separation efficiency. All the resins were washed with hot 4 *N* HCl and then with distilled water to remove excess acid prior to use.

Eluent

A 0.02 *M* solution of DTPA buffered to pH 8 with ammonium hydroxide was employed for eluting the rare earth. Eluent flow was maintained at 1 to 1.5 ml/min. Deaerated solutions were used for the higher temperature experiments.

Stock Solutions

To facilitate the analyses of the eluted fractions, a synthetic 3% doped oxide mixture of dysprosium, europium, gadolinium, and terbium in yttrium oxide was investigated. Data obtained from these experiments were used to select the resin later employed in the purification of commercial-grade yttrium oxide.

SEPARATION PROCEDURE

The rare-earth oxides are dissolved in 3 ml of 3 *N* HCl and added to the column with as little agitation of the resin as possible. The column is washed with distilled water until free of acid, as indicated by pH and chloride tests. Buffered DTPA is then added to the column and the eluted fractions collected.

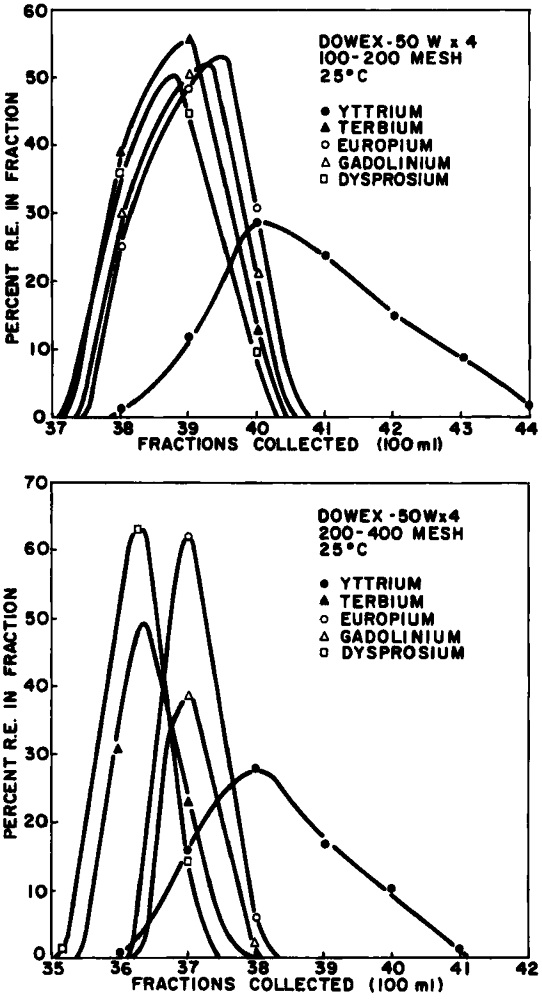

FIG. 1. Comparison of resin particle size.

ELEVATED-TEMPERATURE EXPERIMENTS

Electrically heated columns were found to be an improvement over previous methods using steam. Powerstats were used for accurate temperature control. The results showed that heat was more uniformly distributed throughout the resin and less bubble formation was encountered. Electrically heated columns were therefore

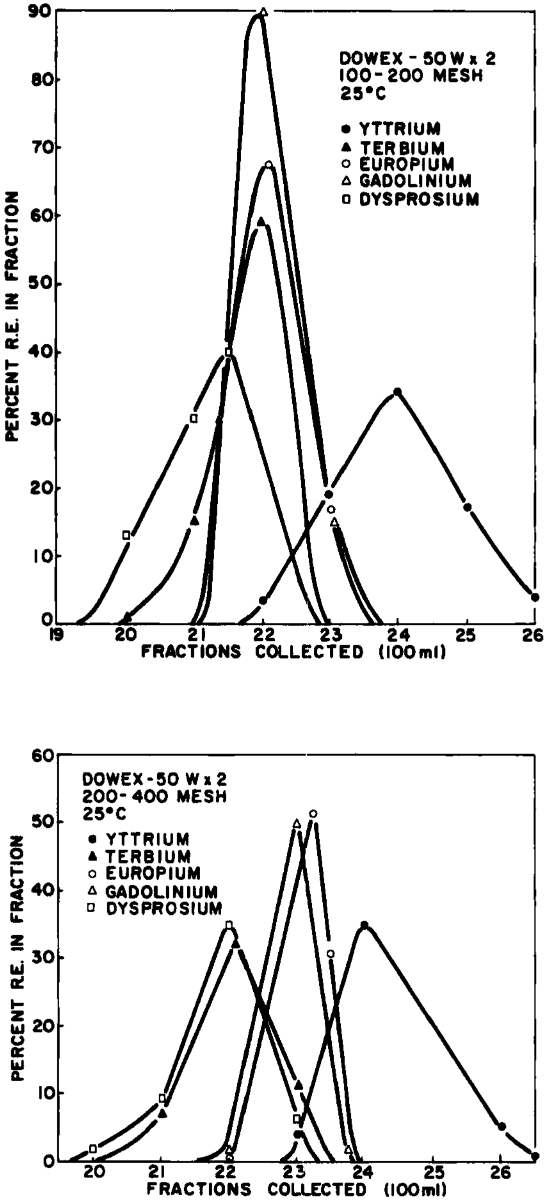

FIG. 2. Comparison of resin cross-linking.

employed for all elevated temperature experiments reported in this paper. Column surface temperatures were measured with an iron constantan thermocouple taped to the outside of the column and insulated with asbestos cloth.

ANALYSIS

Effluents collected from the doped Y_2O_3 were analyzed by X-ray fluorescence. In the commercial mixtures the rare earths were precipitated as the oxalates, ignited to oxides in crucibles at 1200°C for 8 hr, and analyzed by emission and mass spectroscopy.

RESULTS AND DISCUSSION

The results of the analysis indicate that there is an improved separation of yttrium from the rare earths. Figure 1 shows that a

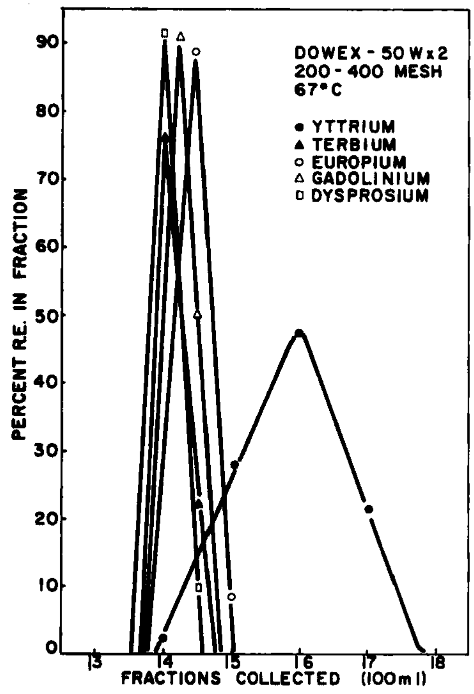

FIG. 3. Rare-earth elutions at elevated temperatures.

TABLE 1

Analysis of Fractions from Ion-Exchange Columns
(ppm by weight)

Impurity	Fractions 1 to 33	Fractions 34 to 50	Fractions 51 to 55
La	<1	<1	1070
Ce	<1	<1	1140
Pr	<1	<1	860
Nd	<4	<1	5400
Eu	10	<1	<3
Sm	115	<1	9
Gd	104	2	19
Tb	52	<1	<6
Dy	1295	<1	<7
Ho	186	<1	<2
Er	620	<1	<4
Tm	135	<1	<1
Yb	580	<1	<4
Lu	21	<1	<1
Th	<2	<1	<2

greater separation occurs when a smaller particle size of resin is used. Decreased cross-linking of the resin also improves the separation, as shown in Fig. 2. When elutions were carried out at elevated temperatures, a further improvement was noted, as shown by the sharper elution curves in Fig. 3. The curves indicate the percentage of the initially added rare earth which elutes per fraction.

To avoid bubble formation in columns at elevated temperatures, thoroughly deaerated solutions must be used in preparing the resin as well as the eluent. In addition, preheaters were employed in our experiments to reduce the readsorption of air during elution.

Removal of rare-earth impurities from commercial-grade yttrium oxide was performed using DTPA and Dowex 50W × 2, 200–400 mesh resin at both room temperature and 70°C. The results of analyses show that separation efficiency is improved at higher temperatures. As shown in Table 1, analysis of the early fractions (1–33) shows heavy rare-earth contamination, while the light rare earths are found in the tail-end fractions (51–55).

A comparison of a typical mass spectrographic analysis of yttrium oxide before and after purification in the largest column is shown

TABLE 2

Purification of Y_2O_3 by Ion Exchange

	Impurities (ppm by weight)	
	Before	After
La	5	<1
Ce	6	<1
Pr	4	<1
Nd	25	<2
Eu	10	<1
Sm	9	<2
Gdq	15	<3
Tb	5	<1
Dy	295	<2
Ho	20	1
Er	104	<2
Tm	12	<1
Yb	88	<2
Lu	4	<1
Th	434	<1

in Table 2. The results demonstrate that 99.9999% pure yttrium oxide can be produced by using a smaller particle size resin (200–400 mesh) and lesser cross-linking (2%) than previously reported.

An ion-exchange system capable of operating on a continuous basis has been assembled to supply research quantities of high-purity material. The system consists of four (120 × 6 cm diameter) electrically heated columns with an automatic solution feed system for the eluting agent. Thirty-five grams of highly purified yttrium oxide, suitable for research purposes, can be produced per column.

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