ethylenediamine and for a solution of yttrium acetate in this solvent. Although large quantities of water cause precipitation in this and other comparable systems, as previously noted, reasonable quantities of water can be added. As indicated by the data summarized in Table VI, the presence of water short of precipitation does increase conductance values. Comparison of the values for the pure solvent with those for the solution suggests that improved conductance in the latter cannot be due to increase in solvent conductance alone. It seems probable that another factor is the replacement of ethylenediamine molecules by water molecules in the solvated cation to give smaller, more mobile species. Comparable observations were made with other rare earth metal salts.

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Quantity Separation of Rare Earths by Liquid–Liquid Extraction. I. The First Kilogram of Gadolinium Oxide[1]

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Countercurrent liquid–liquid extraction techniques have been successfully applied to the separation of large quantities of rare earths—specifically for the purification of gadolinium. The solvents used were *n*-tributyl phosphate and nitric acid. More than a kilogram of better than 95% gadolinium oxide has been produced. Increases in temperature have been found to decrease extraction into the organic phase. Distribution coefficients of rare earths between freshly prepared tributyl phosphate and nitric acid are nearly independent of rare earth concentration within the practical operating range.

Introduction

Liquid–liquid extraction is theoretically the most promising method of separating rare earths. The chief requirements are that there be adequate differences in distribution factors between successive elements and that it be possible to maintain these differences throughout a multistage countercurrent extraction system. Many investigations have been conducted in this field. Most of them have remained unpublished because separation factors were too small or individual distribution coefficients were too small or too large. Appleton and Selwood[2] expressed interest in developing a process for which the separation factor between neodymium and lanthanum was only 1.06. Templeton and Peterson[3] obtained a factor of 1.5 between these elements by extraction with hexanol from nitrate solutions, but individual extraction coefficients were small. The claims of Fischer, Dietz and Jübermann[4] in 1937 that numerous combinations of salts and solvents gave separation factors of 1.5 between adjacent elements do not agree with the experience of other workers and these authors have never given any concrete evidence of such success. A 1950 review by Bock,[5] of Fischer's laboratory, dismisses extraction methods with pessimism.

The observations of Peppard,[6] *et al.*, were far more promising. They reported that by the use of tributyl phosphate and 12 *N* nitric acid, separation factors of about 2 between adjacent elements were attained, and distribution coefficients were satisfactory for operation of standard extraction equipment. While their work was all done on a tracer or small batch level and included only a few of the rare earths, it was evident that the process could be applied to a continuous countercurrent system for the separation of all of these elements.

The present authors had need of kilogram quantities of each of several of the elements with high purity for use in the electromagnetic separation of their isotopes. Only lanthanum, cerium, neodymium and samarium were readily available in sufficient quantities. The expense and labor necessary to produce the others by conventional methods were prohibitive. Therefore, development of the extraction process was undertaken to supply these needs. Special attention was given first to gadolinium, the most abundant of the remaining elements. The separation was approached as a production problem, with investigation of details of extraction characteristics being limited to the solution of specific problems encountered as the work progressed.

Experimental

Batch Countercurrent Fractionation.—A pseudo-countercurrent batch system was set up consisting only of beakers with drains and motor driven stirrers. The organic solvent was always a 60:40 mixture of tributyl phosphate and Varsol,[7] equilibrated with concentrated nitric acid. With other conditions fixed, the point at which a mixture of rare earths is divided is dependent only upon the ratio of the volumes of organic and aqueous solvents used. Purification of a single element requires separation first on one side of it, then on the other.

The first aim was to split the mixture between samarium

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, September, 1952.

[2] D. B. Appleton and P. W. Selwood, THIS JOURNAL, **63**, 2029 (1941).

[3] C. C. Templeton and J. A. Peterson, *ibid.*, **70**, 3967 (1948).

[4] W. Fischer, W. Dietz and O. Jübermann, *Naturwissenschaften*, **25**, 348 (1937).

[5] R. Bock, *Angew. Chem.*, **62A**, 375 (1950).

[6] D. F. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.*, **57**, 294 (1953).

[7] Varsol is the trade name of a petroleum fraction similar to kerosene but purified from gasoline. It does contain unsaturated hydrocarbons.

and gadolinium. The europium content of the material was so low that it could be ignored. Subsequent extraction of the fraction containing most of the gadolinium with a different solvent ratio brought about a division between gadolinium and terbium. Results of three production experiments are given in Table I.

TABLE I

Experiment	1			2			3		
	Feed	Aqueous	Organic	Feed	Aqueous	Organic	Feed	Aqueous	Organic
Wt. of oxide, (g.)	500	100	400	3600	1900	1700	1600	1050	550
Analyses (%)									
Nd_2O_3	10	50		2	2		2	3	
Sm_2O_3	51	50	51	35	64	2	59	86	8
Gd_2O_3	31		39	48	34	64	38	11	90
YE_2O^3[a]	8		10	15		34	1		2
Separation factor[b]				Gd/Sm = 60			Gd/Sm = 88		

[a] YE includes yttrium and all elements above gadolinium. [b] Separation factor is the ratio of one element to another in one fraction divided by the ratio of these elements in the other fraction.

The feed solution was made up by dissolving 160 g. of oxide in each liter of 15.6 N nitric acid. The concentrated acid was used also for the aqueous scrubbing solution. Relative volumes of feed, aqueous and organic were 1:4:4 for the first experiment and 1:1.67:4 for the others.

In the first experiment there were four stages on either side of the center feed, in the others nine stages on either side. The table includes gadolinium–samarium separation factors attained in two experiments. It is evident that, while division was made in the intended place, the anticipated number of actual stages was not realized. A theoretical single stage should give a separation factor of at least 3 between these elements at the acidity used. The relatively large volumes of feed solution necessary to obtain any capacity of throughput in the system caused an imbalance between its two sides and invalidated the square root rule.[8] However, its operation did produce a considerable quantity of material well depleted in samarium. The symbol YE in the analyses designates yttrium and all elements above gadolinium.

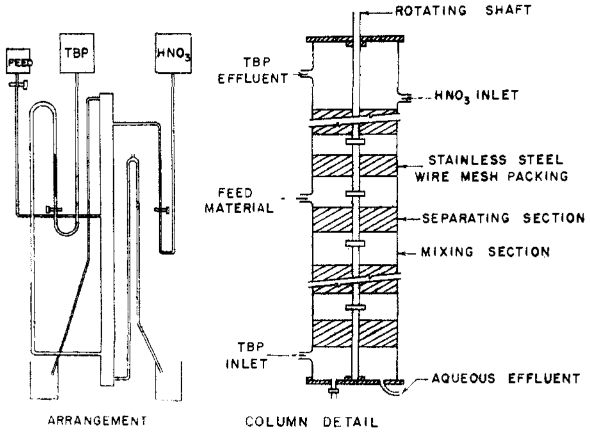

Fig. 1.—York–Scheibel extraction apparatus.

Analyses were made by optical spectroscopy, using a porous cup method developed at Oak Ridge National Laboratory.[9] The values given are approximate averages of samples taken during the experiments. In the work described this far, no satisfactory determinations of elements above gadolinium were obtained because of the lack of suitable standards. Later analyses were extended to other elements as standards were obtained through purchase or through fractional precipitations and ion exchange separations at the laboratory.

Continuous Countercurrent Fractionation.—At this point batch operations were replaced by application of a small laboratory York–Scheibel extraction column. This apparatus is shown schematically in Fig. 1. The 1-inch column has 11 mechanical stages with a stirrer–propellor in each $^1/_2$ inch mixing section. Controlled countercurrent flow is attained by introducing the organic solvent through a rotameter into the bottom of the column. The aqueous scrubbing phase enters the topmost section in like manner. The aqueous feed is introduced into the center stage.

This column did not give 11 actual stages. Even at maximum speed, the agitators did not accomplish complete mixing of the liquids used. Separation of the phases took place in a small fraction of the available space. Results obtained indicated that only about 3 or 4 theoretical stages were realized. An unknown part of this deficiency was certainly due to the fact that the relative conditions in the two parts of the column were not ideal.

In Table II are results of three production experiments with this equipment. These illustrate two divisions on the terbium side of gadolinium and one on the samarium side. Flow rates for feed, aqueous, and organic were in the approximate ratios of 1.5:1:1, 2:1:1 and 1.5:1:2 for the three successive experiments. Total flow was 1300 to 1700 ml. per hour. The feed contained 20 g. of rare earth oxide per liter. The aqueous solution was 10 N nitric acid while the feed was in 13 N nitric acid, thus compensating for the difference in solvent ratios in the two arms of the column by an inverse difference in distribution coefficients. The organic solvent, 60:40 tributyl phosphate–Varsol, was equilibrated with 12 N nitric acid.

TABLE II

Experiment	4			5			6		
	Feed	Aqueous	Organic	Feed	Aqueous	Organic	Feed	Aqueous	Organic
Wt. of oxide, g.	1423	893	530	863	546	317	475	43	432
Analyses (%)									
Sm_2O_3	2	3		3	5		7	45	4
Gd_2O_3	63	85	34	84	93	71	90	55	93
Tb_4O_7	7	4	10	7	2	12	2		2
Dy_2O_3	17	7	36	5		15	1		1
YE_2O_3[a]	11	1	20	1		2			
Separation factor	Tb/Gd = 6			Tb/Gd = 8			Gd/Sm = 19		

[a] YE here includes yttrium and all elements above dysprosium.

With a few additional extractions most of the gadolinium in the concentrates was obtained in a few batches totaling more than a kilogram and having gadolinium oxide contents from 95 to 98%. The chief impurity was terbium, which is not very objectionable in the separation of gadolinium isotopes.

Recently a large quantity, 125 kilograms, of 25% gadolinium oxide was obtained, and the extraction column is now being operated as a research instrument to determine

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(8) For maximum mutual separation between elements x and y, the following conditions should be met in the system

$$(\mathrm{Vol_b}/\mathrm{Vol_a}) \times K_x > 1$$
$$(\mathrm{Vol_b}/\mathrm{Vol_a}) \times K_y < 1$$
$$(\mathrm{Vol_b}/\mathrm{Vol_a}) = 1/\sqrt{K_xK_y}$$

where $\mathrm{Vol_a}$ and $\mathrm{Vol_b}$ are relative volumes of organic and aqueous phases, and K_x and K_y are distribution coefficients for the two elements between the two solvents.

(9) J. A. Norris and C. E. Pepper, *Anal. Chem.*, **24**, 1399 (1952).

the optimum conditions for its separation into the various elements present. It is planned to do the actual production of the more abundant earths on a larger and theoretically more effective column.

Factors Affecting Extraction.—Because temperature variations in the laboratory were suspected as a disturbing influence on the separations, distribution coefficients between 60% tributyl phosphate and 12 *N* nitric acid were determined for neodymium and samarium at 3 different temperatures and various concentrations of the elements. A constant temperature bath was used for these small scale experiments.

The data are in Fig. 2. It is seen that an increase in temperature definitely decreases the extraction coefficients at all concentrations studied. On the other hand the concentration of rare earth apparently has little effect throughout this range. The slight variation of distribution coefficients with concentration may be a function of the total nitrate concentration rather than the rare earth concentration. The experiments were designed in such a way that acid concentration remained constant when rare earth concentration was changed.

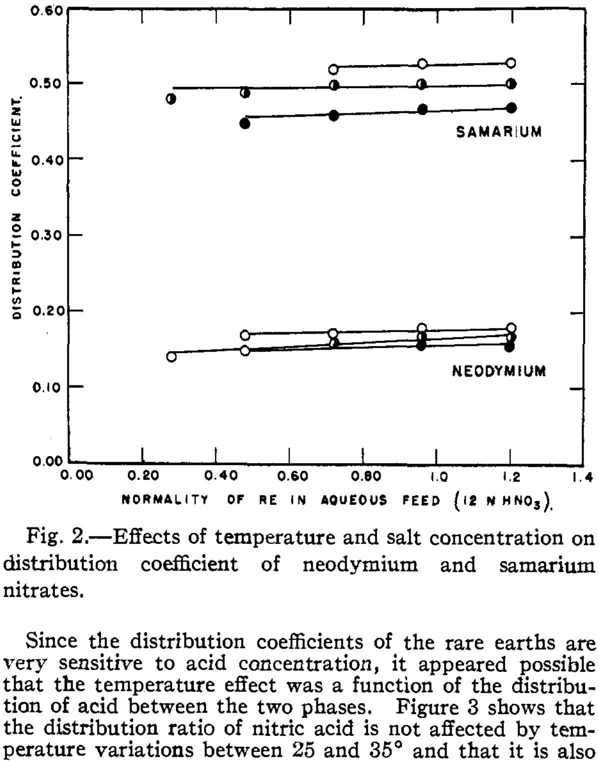

Fig. 2.—Effects of temperature and salt concentration on distribution coefficient of neodymium and samarium nitrates.

Since the distribution coefficients of the rare earths are very sensitive to acid concentration, it appeared possible that the temperature effect was a function of the distribution of acid between the two phases. Figure 3 shows that the distribution ratio of nitric acid is not affected by temperature variations between 25 and 35° and that it is also apparently independent of the acid concentration from 12 to 15 *N*. The normality of acid in the organic phase is approximately 0.25 times that in the aqueous phase under all conditions studied.

Discussion

It is certain that the separations attained here were far short of the maximum possible, since they were made under conditions that were not ideal, and in every case they were the results of exploratory work. A far better batch system could be devised on the basis of present knowledge. Separations on the column were necessarily broken up into eight-hour periods, with consequent upsetting of equilibrium conditions each day. Operations were performed with room temperature variation from 15 to 40°. Control of flow rates required frequent adjustment of valves and stopcocks in accordance with measured flows, since temperature variations changed the viscosities of the liquids and made rotameter calibrations inaccurate. Individual distribution coefficients were obtained with freshly prepared solvent. The effects of aging and of contact with the constituents of a continuously operated countercurrent system are the subjects of an investigation now in progress.

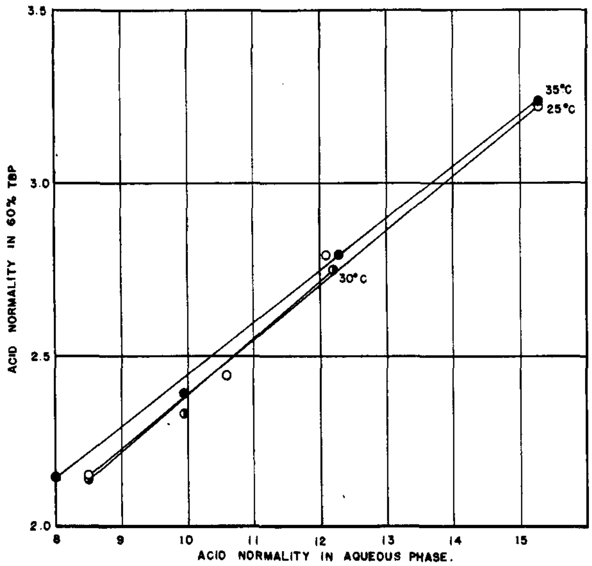

Fig. 3.—Effects of temperature and acidity on distribution of nitric acid.

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