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LIQUID-LIQUID EXTRACTION OF NEODYMIUM AND SAMARIUM NITRATES

By

A. C. Topp

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LIQUID-LIQUID EXTRACTION OF NEODYMIUM AND SAMARIUM NITRATES

A. C. Topp

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ABSTRACT

A preliminary study has been made of the distribution of neodymium and samarium nitrates between 12N nitric acid and tributyl phosphate diluted with Varsol. There is a nearly constant separation factor of 2.8 between these two elements. Distribution coefficients are dependent upon temperature but not upon rare earth concentration. The use of the solvent in an extraction column increases distribution coefficients by a definite amount. Attempts to determine the mechanism have been unsuccessful.

LIQUID-LIQUID EXTRACTION OF NEODYMIUM AND SAMARIUM NITRATES

A. C. Topp

The program of the Stable Isotope Research and Production Division of Oak Ridge National Laboratories includes the production of the isotopes of the rare earth elements. A necessary preliminary problem is the separation of the rare earth elements. The procedure adopted for the separation was liquid-liquid extraction using as solvents, nitric acid and a mixture of Varsol and tributyl phosphate. The separation has reached the pilot plant state, using a Scheibel countercurrent extraction column.

The purpose of the work reported herein was to determine fundamental data on the process. Neodymium and samarium are representative rare earth elements and were available in quantity as the pure oxides. They were used in the form of the nitrates as the materials in the extraction experiments. The solvents used in the extractions were 12 normal nitric acid and a mixture of 40% Varsol-60% tributyl phosphate as they were representative of the solvents used in the Scheibel column. Other conditions, as concentration and temperature, were treated as variables and were changed during the investigations.

EXPERIMENTAL

Solutions

Rare Earth Nitrate Solutions

Stock solutions of neodymium and samarium nitrates of a concentration of approximately 1.2 normal were prepared in 12.3 and 12.5 normal nitric acid, respectively. Solutions of the nitrates of 0.96, 0.72, 0.48 and 0.24 normality were made by diluting the stock solutions with 12.3 normal nitric acid. The actual normalities of the stock solutions of neodymium and samarium nitrates were 1.17 and 1.18, respectively, as determined from the weights of the recovered oxides in the extraction experiments.

Organic Solvent

The organic solvent used in the extraction experiments was a 40% Varsol-60% tributyl phosphate mixture. It was conditioned by washing once with 5% sodium carbonate solution, four times with water and twice with 12.3 normal nitric acid. It was found that two washes with acid were sufficient to establish equilibrium between the acid and the organic phase. The volume of organic solvent was measured after equilibration.

Column Organic

Samples of the organic solvent were obtained from that being used continuously in the Scheibel Extraction Column for some time.

Nitric Acid

Nitric acid solutions were prepared by diluting Bakers Reagent Nitric Acid. The rare earth nitrate solutions were diluted with 12.3 normal nitric acid prepared by diluting 780 ml of the concentrated acid to one liter. The medium for the neodymium nitrate, thus, remained the same and for the samarium nitrate approximately so.

PROCEDURE

In order to determine if there were a temperature effect on the distribution coefficients of the rare earth nitrates, the extractions were made in a constant temperature bath. The bath settings were 25.0° C, 30.2° C and 34.9° C.

Twenty-five ml of the salt solution and 25 ml of the equilibrated organic solvent were placed in tall-form beakers in the bath. The mixtures were mechanically stirred for approximately one minute.

The mixtures were transferred to separatory funnels in the bath and allowed to separate.

The aqueous and organic phases were drawn off. The rare earth nitrates in the organic phase were washed out with water. These and the rare earth nitrates in the aqueous phase were precipitated as oxalates, ignited, and weighed as oxides.

Following the investigation of the effect of temperature on the distribution coefficients the procedure was modified. Extractions were carried out at 30.2°C. The solutions were placed in separatory funnels in the constant temperature bath. When temperature equilibrium had been established the funnels were removed from the bath and shaken manually for one minute. The funnels were returned to the bath for the layers to separate. The subsequent steps were the same.

Duplicate samples were treated by the two methods and the distribution coefficients were in agreement.

The distribution coefficients of hydrogen nitrate between the aqueous and organic phases were determined by the method of mechanical stirring. Aliquots of the two phases were titrated with standard sodium hydroxide solution to determine the nitric acid content of each. The nitric acid in the organic phase was extracted by mixing the aliquot with a relatively large volume of water. The presence of the organic solvent did not interfere with the titration.

RESULTS

Distribution Coefficients of Neodymium Nitrate, Samarium Nitrate and Hydrogen Nitrate

Effect of Temperature and Concentration on the Distribution Coefficients of Neodymium and Samarium Nitrates between 12.3N Nitric Acid and 40% Varsol-60% Tributyl Phosphate

The distribution coefficients of neodymium nitrate between 12.3N nitric acid and 40% Varsol-60% tributyl phosphate at 25.0°C, 30.2°C and 34.9°C are given in Table I and those of samarium nitrate under the same conditions in Table II.

TABLE I

DISTRIBUTION COEFFICIENTS OF NEODYMIUM NITRATE, R o/a *

	Normality of $Nd(NO_3)_3$ in Feed				
Temperature °C	1.2N	0.96N	0.72N	0.48N	0.24N
25.0	0.18	0.18	0.17	0.17	-
30.2	0.17	0.17	0.16	0.15	0.14
34.9	0.16	0.16	0.16	0.15	-

* R o/a is defined as the ratio of the concentration of the solute in the organic layer to its concentration in the aqueous layer.

TABLE II

DISTRIBUTION COEFFICIENTS OF SAMARIUM NITRATE, R o/a

Temperature °C	Normality of $Sm(NO_3)_3$ in Feed 1.2N	0.96N	0.72N	0.48N	0.24N
25.0	0.53	0.53	0.52	0.55	-
30.2	0.50	0.50	0.50	0.49	0.48
34.9	0.47	0.47	0.46	0.45	-

The effects of changing temperature and concentration of the distribution coefficients of neodymium and samarium nitrates, though small, show definite trends. The value for the distribution coefficient decreases with decreasing concentration of the salt and decreases with increasing temperature.

The temperature and concentration effects might have an explanation on the basis of a change of nitrate ion concentration in the two phases. The distribution coefficient of hydrogen nitrate between the aqueous and organic phases might change with temperature and, hence, change the distribution coefficient of the rare earth salt. Secondly, with decreasing salt concentration at constant nitric acid concentration, the total nitrate in the system decreases. It might be that at lower nitrate concentration less nitrate ion distributes in the organic phase and decreases the tendency for the rare earth salt to dissolve in that phase.

The effect of changing nitrate ion concentration was investigated by using mixtures of neodymium and samarium nitrates. The effect of temperature on the distribution coefficients of hydrogen nitrate was determined under different conditions of concentration and temperature.

Distribution Coefficients of Mixtures of Neodymium and Samarium Nitrates

Mixtures of the 1.2 normal stock solutions of neodymium and samarium nitrates were prepared to give concentrations of the individual salts for which distribution coefficients had previously been determined, i.e. 0.96, 0.72, 0.48 and 0.24N. Distribution coefficients between equal volumes of 12.3 normal nitric acid and 40% Varsol-60% tributyl phosphate at 30.2°C were found for the mixtures from the weights of the mixed oxides that were obtained from the two phases. Distribution coefficients were calculated from the weights of oxide obtained when the distribution coefficients were determined for the salts separately at the given concentrations. The results are shown in Table III.

TABLE III

DISTRIBUTION COEFFICIENTS OF MIXTURES
OF NEODYMIUM AND SAMARIUM NITRATES

Solution	R o/a exptl.	R o/a calc.
0.24N $Nd(NO_3)_3$ & 0.96N $Sm(NO_3)_3$	0.43	0.41
0.48N $Nd(NO_3)_3$ & 0.72N $Sm(NO_3)_3$	0.37	0.34
0.72N $Nd(NO_3)_3$ & 0.48N $Sm(NO_3)_3$	0.30	0.28
0.96N $Nd(NO_3)_3$ & 0.24N $Sm(NO_3)_3$	0.24	0.22

The greater values for the distribution coefficients for the mixtures than for the salts, determined separately, indicates the possibility of greater concentration of nitrate ion being the influencing factor.

Effect of Temperature and Concentration on the Distribution Coefficient of Hydrogen Nitrate in 40% Varsol-60% Tributyl Phosphate

Distribution coefficients were determined for hydrogen nitrate between 40% Varsol-60% tributyl phosphate and the aqueous phase. In this case the organic solvent was not treated with sodium carbonate and water before use. The determinations were at 25.0, 30.2 and 34.9 degrees Centigrade, using various concentrations of nitric acid.

Equal volumes of nitric acid and organic solvent were equilibrated by the method of mechanical stirring. The equilibration was repeated twice until it was established that the nitric acid concentration in the organic phase was the same for the second and third steps. The third equilibration was, therefore, discontinued. The nitric acid in each phase was determined by titration with standard sodium hydroxide solution.

A volume increase in the organic phase was noted in the first equilibration, but a further change in volume could not be detected in the second step.

The distribution coefficients for hydrogen nitrate and related data are summarized in Table IV.

TABLE IV

DISTRIBUTION COEFFICIENTS OF HYDROGEN NITRATE
IN 40% VARSOL-60% TRIBUTYL PHOSPHATE

Temperature	Normality HNO_3 in Aqueous	Normality HNO_3 in Organic	R o/a	Increase Volume Organic, %
25.0°C	15.3	3.62	0.24	17
	12.1	2.79	0.23	12
	10.6	2.44	0.23	10
	8.5	2.15	0.25	8
30.2	15.3	-	-	16
	12.2	2.75	0.23	10
	9.95	2.33	0.23	10
	8.5	2.14	0.25	8
34.9	15.3	3.64	0.24	16
	12.3	2.79	0.23	12
	9.95	2.39	0.24	8
	8.0	2.14	0.27	8

The constancy of the distribution coefficients of hydrogen nitrate under changes of temperature would remove consideration of its behavior as an explanation for the changes in the distribution coefficients of neodymium and samarium nitrates with changes of temperature.

Distribution Coefficients of Neodymium and Samarium Nitrates in Organic Solvent Used in Scheibel Column

The distribution coefficients for neodymium and samarium nitrates reported in Tables I and II are not in agreement with those found by F. A. Kappelmann, whose values were 0.5 and 1.3, respectively, under similar conditions.

Two differences in procedure were noted. In the present work the volume of organic solvent was measured after equilibrating with nitric acid, while Kappelmann measured his volume of organic solvent before treating with sodium carbonate, water and nitric acid. As shown in Table IV, equilibrating the organic solvent with nitric acid leads to an increase in volume of the organic solvent of 10 to 12 per cent for 12

normal acid. Distribution coefficients based on the volume of unequilibrated organic solvent would be expected to be greater to the same degree as the increase in volume. Secondly, the organic solvent used to determine the distribution coefficients of Tables I and II was from a stock solution of 40% Varsol-60% tributyl phosphate, a fresh sample of which was treated with sodium carbonate and water and equilibrated before each determination. Kappelmann's organic solvent was from the material used for a long period in the Scheibel column. It had gone repeatedly through the cycle of use in the column, washing with water to remove the rare earth nitrates and nitric acid, reequilibrating with nitric acid and reusing in the column. Other conditions used by Topp and Kappelmann, i. e. temperature, concentration of rare earth nitrates, concentration of nitric acid, nominal ratio of Varsol to tributyl phosphate, and manipulation, were approximately the same.

Investigations were made to reconcile the divergent results, mainly from the point of view that continuous use of the organic solvent in the column had brought about a chemical or physical change in the composition of the solvent.

Distribution Coefficients of Neodymium and Samarium Nitrates in Column Organic Solvent

Samples of organic solvent being used in the column were obtained. They were equilibrated with 12. 3 normal nitric acid and used to obtain the distribution coefficients of neodymium and samarium nitrates. The results are shown in Table V, together with the distribution coefficients for fresh solvent and Kappelmann's earlier results.

TABLE V

DISTRIBUTION COEFFICIENTS OF NEODYMIUM AND SAMARIUM NITRATES IN FRESH AND COLUMN ORGANIC SOLVENT, R o/a

Feed (in 12.3 acid)	Fresh Solvent	Column Organic Kappelmann	Column Organic Topp
1.2N $Nd(NO_3)_3$	0.17	0.5	0.46(a)
1.2N $Sm(NO_3)_3$	0.50	1.3	1.26(a)
1.2N $Sm(NO_3)_3$			1.36(b)

(a) sample obtained 9-8-52

(b) sample obtained 9-15-52

The agreement in the distribution coefficients of Kappelmann and Topp for column organic solvent and the differences for both with those obtained with the fresh solvent indicate that there is a marked difference in the properties of the two solvents. The differences might be brought about by chemical reaction in the mixture of Varsol, tributyl phosphate, nitric acid, water, and rare earth salts, or by physical action incurred during the continual use of the solvent mixture.

Distribution Coefficients in Cleaned Column Organic Solvent

A possible chemical reaction to explain the greater extraction efficiency of the column organic solvent might be the formation of dibutyl and monobutyl phosphates by hydrolysis of tributyl phosphate due to the constant contact with water. These, if present, should be removed by washing with sodium carbonate or sodium hydroxide solutions.

Part of the sample of column organic solvent, obtained 9-8-52, was washed three times with 5% sodium carbonate, four times with water, and twice with 12.3 normal nitric acid. Distribution coefficients were determined for neodymium and samarium nitrates from 1.2 normal solutions in 12.3 normal nitric acid.

Column organic solvent, obtained 9-15-52, was washed with sodium hydroxide solution, water, and 12.3 normal nitric acid and the distribution coefficient for samarium nitrate from 1.2 normal solution in 12.5 normal nitric acid was determined. On the first washes with sodium hydroxide solution the aqueous layer developed a bright yellow color. Washing with sodium hydroxide was continued until the layer was colorless. This required five washes.

A summary of the results of the above experiments is given in Table VI.

TABLE VI

DISTRIBUTION COEFFICIENTS OF NEODYMIUM AND SAMARIUM NITRATES IN CLEANED COLUMN ORGANIC SOLVENT, R o/a

Feed	Unwashed Column Organic	Na_2CO_3 Wash	NaOH Wash
1.2N $Nd(NO_3)_3$	0.46	0.45	-
1.2N $Sm(NO_3)_3$	1.26	1.28	-
1.2N $Sm(NO_3)_3$	1.36	-	1.38

It is to be concluded from the agreement between the values for the distribution coefficients obtained for the washed and unwashed column organic solvent that the difference in extraction efficiency of pure organic solvent and column organic solvent is not due to the presence of di- and monobutyl phosphates in the latter.

Change in Distribution Coefficient of Neodymium and Samarium Nitrates with Change in Varsol-Tributyl Phosphate Ratios

Distribution coefficients of neodymium and samarium nitrates from 1.2 normal solutions in 12.3 normal nitric acid were determined with freshly prepared organic solvents in which the ratios of Varsol to tributyl phosphate were varied. The extractions were carried out at 30.2°C using 25 ml each of the aqueous feed and organic solvent, which had been treated with sodium carbonate solution, water and 12.3 normal nitric acid. The results are given in Table VII and are shown graphically in Figure 1.

TABLE VII

DISTRIBUTION COEFFICIENTS OF NEODYMIUM AND SAMARIUM NITRATES IN ORGANIC SOLVENTS OF VARYING COMPOSITION

Varsol-Tributyl Phosphate	R o/a $Nd(NO_3)_3$	R o/a $Sm(NO_3)_3$	R Nd/R Sm
40 - 60	0.17	0.50	0.34
25 - 75	0.27	0.76	0.36
15 - 85	0.36	0.97	0.37
0 - 100	0.53	1.47	0.36

It was proposed that the higher values for the distribution coefficients in the column organic solvent might be due to loss of Varsol from the mixture due to chemical or physical action. Locating the values for the distribution coefficients for neodymium and samarium nitrates in column organic solvent, namely 0.46 and 1.26, respectively, (Table V) on the curves of Figure 1, would require the composition of the organic solvent to be approximately 94% tributyl phosphate. This appears to be an excessive loss of Varsol from the mixture. It was noted, however, that in washing the column organic solvent, emulsification occurred to an extent similar to that in mixtures of fresh organic solvent of small Varsol content.

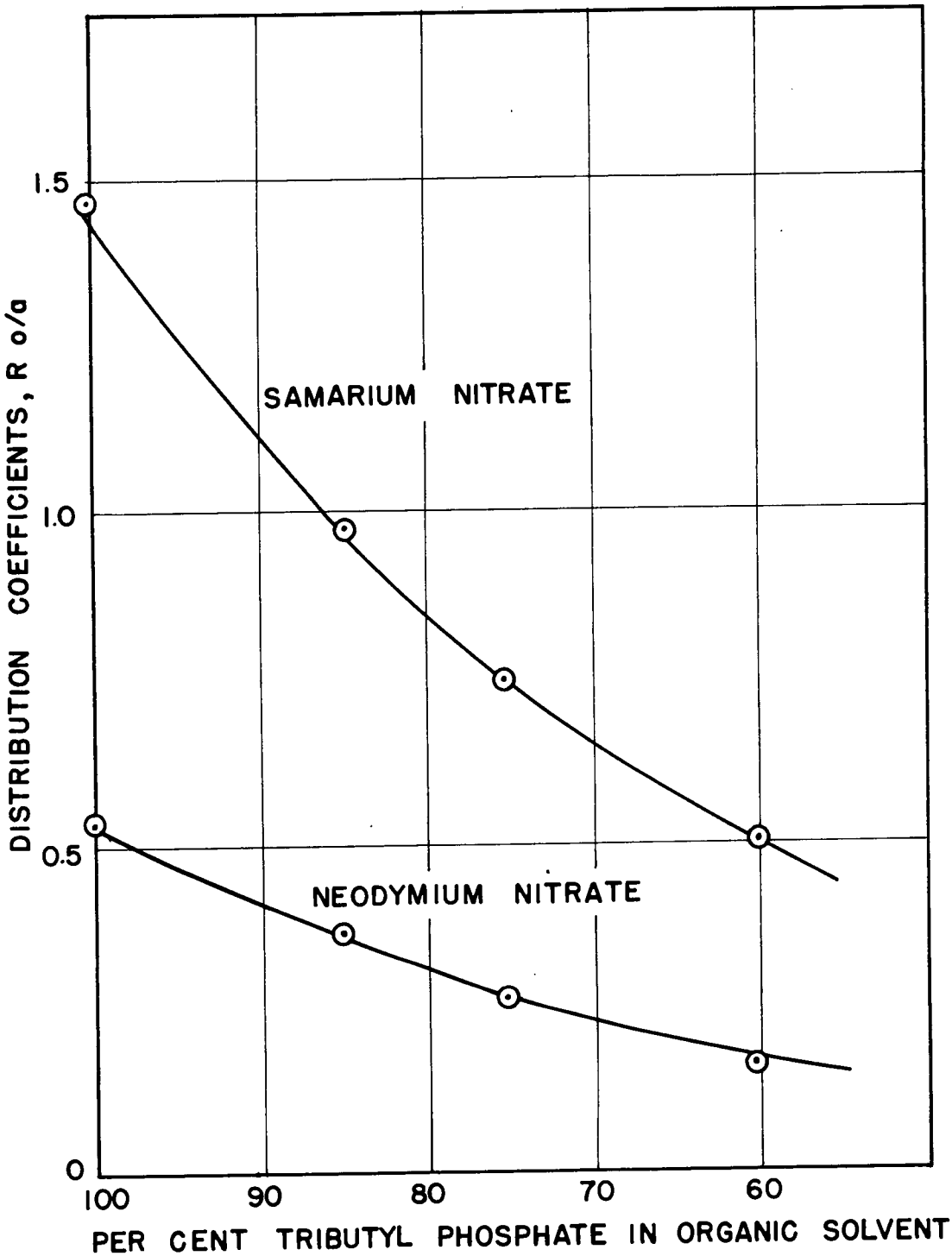

FIGURE 1. EFFECT OF DILUTION OF TRIBUTYL PHOSPHATE ON EXTRACTION OF NEODYMIUM AND SAMARIUM NITRATES

Effect of Time on Nitric Acid Content of Organic Solvent

The effect of continuous contact between nitric acid and organic solvent was determined by following the change in the normality of the acid dissolved in the organic solvent over a period of time.

A sample of 40% Varsol-60% tributyl phosphate was washed with sodium carbonate and water and equilibrated with 12.3 normal nitric acid. It was stored in a stoppered flask for five days at 25.0°C and samples were withdrawn periodically for titration with standard sodium hydroxide solution. After the five day period it was stored at room temperature. Table VIII gives the normalities of the nitric acid in the organic solvent after the specified elapsed times of contact.

TABLE VIII

CHANGE OF NORMALITY OF NITRIC ACID DISSOLVED IN ORGANIC SOLVENT WITH TIME

Time of Contact	Normality Nitric Acid in Organic Solvent
0	2.75
1 day	2.63
2 days	2.45
5 days	2.32
14 days	1.96
46 days	1.92

A second sample of 40% Varsol-60% tributyl phosphate was reequilibrated a number of times for a period of two weeks. The normality of the nitric acid in the organic solvent was determined before and after reequilibration. It was found that before reequilibration the acid content had fallen to approximately 2.6 normal and that after reequilibration it had been restored to approximately 2.8 normal.

Effect on Distribution Coefficients of Age of Organic Solvent

Concurrent with the determination of the effect of time on the nitric acid content of aging organic solvent, samples of the same organic solvent were used to obtain the distribution coefficients of neodymium and samarium nitrates from 1.2 normal solutions in 12.3 normal acid at 30.2°C. Solvent "A" was reequilibrated before each

distribution coefficient determination. Sample "B" had been standing after equilibration for 46 days and was then reequilibrated with 12.3 normal nitric acid for the distribution coefficient determination. The results of these experiments are given in Table IX. They show no detectible effect due to the age of the organic solvent on the value of the distribution coefficients of the two salts.

TABLE IX

DISTRIBUTION COEFFICIENTS OF NEODYMIUM AND SAMARIUM NITRATES WITH AGING ORGANIC SOLVENT

Solvent	Time	R o/a $Nd(NO_3)_3$	R o/a $Sm(NO_3)_3$
A	0	0.18	0.50
A	1 day	0.18	0.49
A	2 days	0.17	0.49
A	3 days	0.18	0.48
A	7 days	0.18	0.49
A	25 days	0.19	-
B	46 days	0.18	-

CONCLUSIONS

The following is a summary of the results obtained in the investigations reported above.

Distribution coefficients of neodymium and samarium nitrates between 12 normal nitric acid and 40% Varsol-60% tributyl phosphate were determined.

The distribution coefficients decrease in value with increasing temperature.

The distribution coefficients decrease in value with decreasing concentration of the salt.

The decrease in the distribution coefficients with decreasing concentration of the salt is apparently due to the decrease in total nitrate ion concentration in the solutions.

Distribution coefficients of hydrogen nitrate between nitric acid and 40% Varsol-60% tributyl phosphate were determined over a range of concentrations of nitric acid and of temperature.

The distribution coefficients for hydrogen nitrate were found to have a constant value for the concentrations and temperatures studied. A difference, by a factor of approximately 2.5 to 1, was established in the distribution coefficients of the rare earth nitrates obtained with organic solvent used in the Scheibel column and freshly prepared organic solvent.

Experimental attempts to account for the difference in the extraction efficiency of the two types of solvent were not successful.

The work carried on in the laboratory of the Isotope Chemistry Department of the Stable Isotope Research and Production Division of Oak Ridge National Laboratories was through an appointment as a Research Participant in the program of the Oak Ridge Institute of Nuclear Studies.

The writer wishes to take this opportunity to express his appreciation to Mr. Boyd Weaver and his staff for their help and cooperation which contributed greatly to making the stay with them a pleasant experience. Special thanks are due to Mr. F. A. Kappelmann whose materials and knowledge were drawn on heavily throughout the investigations.