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February 1967

VARIABLES AFFECTING ION EXCHANGE FOR INTER-ACTINIDE SEPARATIONS*

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Abstract—The actinide elements are usually separated by ion exchange. Cation resin and 2-methylactic acid have been studied with respect to the following variables: flow rate, resin-particle diameter, temperature, and column dimensions. Although separation factors remain constant except for temperature, resolution improves with low flow rates, small resin-particle diameters, high temperatures, and long resin beds. Techniques for obtaining small uniform resin particles and for loading samples on resin beds are discussed.

INTRODUCTION

The use of cation-exchange resin and 2-methylactic acid (α -hydroxy-isobutyric acid or "But") as an eluant is the usual procedure for separating the heavy actinide elements.⁽¹⁾ Although separation factors for the various actinide elements are well-known,⁽²⁾ poor resolution may diminish the usefulness of the separation.

Resolution was investigated for the following variables: column dimensions, resin-particle diameter, flow rate, and temperature. In addition, some variables in loading techniques were investigated.

The authors used Cm and Cf as representatives of the heavy actinides and a resolution factor, R, was introduced, which is obtained by dividing the separation between the Cm and Cf by the full width at half maximum of the Cm peak. Accordingly, the larger the numerical value of R, the better the resolution (Fig. 1).

EXPERIMENTAL

General

The elements used as tracers were ^{244}Cm and ^{252}Cf . The eluant was 2-methylactic acid (commonly known as "But") which had been previously cleaned of any contamination by passing it through Dowex 50x4 cation resin. The "But" was diluted to 0.4 M and adjusted to a pH of 4 with NH_4OH . The resin used by the authors was analytical Grade AG 50wx12 cation resin obtained from Bio Rad Laboratories.

The columns used were a "true-bore" glass with a platinum tip giving a drop volume of 13λ . The columns were water jacketed to obtain a temperature stability of $\pm 1^\circ \text{C}$. The resin bed was supported on a 5-mm plug of fine quartz wool and covered with a 2-mm plug of fine quartz wool spaced 2 mm above the resin bed. The resin was converted to the ammonia form and pre-equilibrated with 10 column volumes of "But." One column volume of water was pushed through the column to remove surplus "But" and to keep elution from starting during loading of the tracers.

The tracer activities were loaded from 0.05 ml of 0.05 M HCl. The glass surfaces above the quartz-wool plug, which had been contacted by the tracer solution, were washed with 0.05 ml of 0.05 M HCl followed by 0.1 ml of H_2O . The final wash consisted of 1 ml of "But," which was removed without letting any of this wash solution pass through the column. Fresh "But" was then added to the column and elution started.

A uniform flow rate was obtained by pressurizing the top of the column and the drops of eluted solution were collected on Al discs. The discs were dried and counted for α particles and fission fragments to determine the shapes of the elution curves.

Resin-particle diameters

The resin obtained from Bio Rad Laboratories had the size and distribution shown in Fig. 2. The resin was graded by settling in the apparatus illustrated in Fig. 3. This equipment consists of four different size columns connected together in the order of smaller to larger diameter and filled with a 1 M NH_4Cl solution. A constant volume-flow rate was maintained with a Beckman Solution Metering Pump which recirculated the NH_4Cl solution through a fine

porosity-glass filter. Ungraded resin was placed in the smallest column and resin particles of diminishing sizes were collected in the successive columns. Figure 4 shows the size and distribution after grading.

Graded batches of resin were packed in 2 mm x 5 cm columns and the results are shown in Fig. 5.

Column dimensions

The results of varying column lengths between 3 and 20 cm are shown in Fig. 6. Figure 7 shows the results of varying column diameters from 0.2 to 0.6 cm.

Flow rates

The effect of flow rates from 0.2 to 1.6 ml/cm²-min through the resin bed were examined for three different batches of resin. The results are shown in Fig. 8.

Temperature

Columns were operated at temperatures from 25 to 95°C. Above 65°C two different points could be obtained, depending on whether or not the resin was preboiled. Preboiled resin was obtained by immersing a test tube containing water and resin in boiling water for 5 min. Figure 9 shows the results of two different batches of resin operated at various temperatures.

DISCUSSION

The authors have introduced the term "resolution factor" instead of using percent resolution, because of the difficulty in determining the first drop of the pure eluant. The position of the first pure drop can vary depending on how much resin is converted from the ammonia form to the hydrogen form during loading. The resolution factor is independent of the position of the first eluant drop. Both percent resolution and resolution factor are related to the band width of an element on a column; it is how the band width is affected by the various experimental parameters that is important.

The authors feel that in their investigations the factors that affect the band width can be broken down into three categories: 1) apparent amount of material to be absorbed on the column; 2) the distribution coefficients; and 3) the rate of reaction between the actinide, the resin, and the eluant.⁽³⁾ Some of the experimental variables can cause changes in more than one category.

The first category, the apparent amount of material, can be affected by column dimensions, resin-particle diameter, and perhaps loading technique. Increasing the column diameter (Fig. 6), while holding the length constant, increases the volume of resin and should decrease the band width for other than a massless sample. As no increase in the resolution factor was observed, perhaps a nonplanar flow through the column increased and compensated for the reduced band width. Increasing the column length, as shown by the data (Fig. 7), changes the apparent band width. As the column is increased in length, the band width becomes relatively narrower. The upper curve over most of its length fits the plate theory of ion-exchange chromatography where the resolution is proportional to the square root of the column length.⁽⁴⁾ The lower curve does not fit the plate theory very well, probably because of nonequilibrium conditions. The

flow rate was too high or the resin-particle diameter too large to obtain equilibrium at this temperature.

The second category, distribution coefficient, was affected by changes in temperature. As the distribution coefficient increases (Fig. 10), the amount of resin needed to band the material decreases and the band width decreases (Fig. 9). The distribution coefficients were calculated from the experimental data by the equation⁽⁵⁾

$$v/x = D_r + \epsilon$$

where

v = the eluate volume to the peak

x = the total resin-bed volume

D_r = the volume-distribution coefficient

ϵ = the void fraction of the resin.

The third category, rate of reaction, was affected by temperature, flow rate, and resin-particle diameter. To obtain equilibrium between the actinides, the resin and the eluant, the rate of reaction must be fast enough so that the actinide ion has time to diffuse in and out of the resin particle before the eluant solution has gone by the particle. The upper curve in Fig. 8 shows this effect. As the flow rate increases, the band width remains constant until the flow rate becomes too fast for diffusion in and out of the resin particle. At this point the band width increases and the resolution decreases. The lower curves in Fig. 8 represent experiments that never reached equilibrium, even at the lowest flow rates studied, because the resin particles were too large. Further effects of particle size and temperature are shown in Figs. 5 and 9. In Fig. 5, it is interesting to note, as shown in the lower two points, that

resolution is a function of the largest particles present in the resin, not the average particle size. Reduction in the cross-linkage in the resin should help increase the rate of reaction, if shrinkage of the resin upon addition of the "But," doesn't upset the load band.

The loading technique the authors used was an attempt to band the activity in the flattest, narrowest band possible at the top of the column. The quartz-wool plug above the resin not only keeps the resin bed from being disturbed during loading and subsequent operations, but also keeps the resin from creeping up the walls of the column. Removal of the final wash does not reduce the band width, but does help keep the small amount (~1%) of load material which was not removed from the walls in the first two washes, from ending up in the tail of the elution peaks (Fig. 1). The authors' load technique is also based on running large amounts of highly radioactive solutions through columns where time is important due to peroxide formation.⁽⁶⁾ Peroxide bubbles in the resin will cause channeling and a reduced resolution.

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FOOTNOTES AND REFERENCES

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†International Atomic Energy Agency Fellow from Egypt.

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XBL672-840

Fig. 1. Elution curve

BBH 673-81

Fig. 2. Ungraded resin

BBH 673-80

Fig. 3. Resin-grading apparatus

BBH 673-82

Fig. 4. Graded resin

XBL672-841

Fig. 5. Particle size

XBL672-852

Fig. 6. Column diameter

XBL672-853

Fig. 7. Column length

XBL672-854

Fig. 8. Flow rate

XBL672-855

Fig. 9. Temperature

XBL672-856

Fig. 10. Distribution coefficients

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