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ANION EXCHANGE SEPARATION OF MOLYBDENUM AND TECHNETIUM AND OF TUNGSTEN AND RHENIUM

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ABSTRACT

The present work was designed to meet a need in radiochemistry for the ready separation of molybdenum and technetium and of tungsten and rhenium. The distribution coefficients for these elements on an anion exchange resin have been determined in hydrochloric and nitric acid solutions of varying concentration. These values were used to determine suitable conditions for separating these elements and recovering them in small volumes free of material which would interfere in measuring their activities.

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There is a need in radiochemistry for suitable separations of molybdenum and technetium and of tungsten and rhenium. Such a need may occur in bombardments of molybdenum and tungsten targets and in the separation of some mother-daughter pairs. The solutions containing the separated elements should allow ready evaporation on counting plates and should not contain appreciable amounts of substances which would absorb the radiation or cause loss of activity on being decomposed or fumed. For these reasons such materials as sodium hydroxide, organic acids, salts, perchloric acid, and sulfuric acid should be avoided. The separations should be reasonably fast and not require large volumes of solution. Anion exchange methods using only the readily volatile hydrochloric and nitric acids appeared to offer favorable conditions for these separations, and the present paper reports the results of studies on these systems.

The separation of molybdenum and rhenium by anion exchange, including hydrochloric acid eluants, has been studied by Fisher and Meloche[1] and by Meloche and Preuss.[2]

(1) S. A. Fisher and V. W. Meloche, Anal. Chem. 24, 1100 (1952).

(2) V. W. Meloche and A. F. Preuss, Anal. Chem. 26, 1911 (1954).

These separations used sodium hydroxide, potassium oxalate, and perchloric acid eluants in parts of their schemes. The first two materials cannot be evaporated from a counting plate, and the last causes loss of activity when

it is fumed. Column elutions of molybdenum and tungsten with hydrochloric acid, the latter in a limited range of acid concentration, have been made by Kraus, Nelson and Moore[3] and a qualitative statement regarding the behavior

(3) K. A. Kraus, F. Nelson and G. E. Moore, J. Am. Chem. Soc. 77, 3972 (1955).

of technetium has been made by these authors.

EXPERIMENTAL

Materials and Analyses. Dowex-1 in the chloride form, 250-500 mesh, dried over magnesium perchlorate, and all from one lot, was used for both the batch equilibrations and the column separations in hydrochloric acid. For the batch equilibrations in nitric acid the resin was treated in a column with 2 M nitric acid until a negative test for chloride was obtained in the eluant. The resin was then washed with water and dried over magnesium perchlorate.

Reagent-grade sodium molybdate dihydrate (Baker and Adamson) was used as the source of molybdenum. The polarographic method of Stackelberg, et. al,, as given by Kolthoff and Lingane,[4] was used to analyze the molybdenum

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed. Interscience Publishers, New York and London, p. 613 (1952).

content of the solutions in determining the distribution coefficients, but the spectrophotometric method given by Sandell[5] was used during the column

(5) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, p. 333 (1944).

separation from technetium because of the much lower concentrations in some samples. One-tenth of the quantities recommended in the latter method were used, keeping the concentrations the same. Readings were taken with a Beckman Model DU spectrophotometer.

Fission product Tc^{99} was obtained from the Oak Ridge National Laboratory in the form of potassium pertechnetate having a specific activity of about 20 microcuries per milligram of technetium. All analyses were made by evaporating suitable aliquots on platinum plates and counting in a G-M counter.

The tracer W^{185}, prepared by pile irradiation of tungsten, was obtained from the Oak Ridge National Laboratory as a solution of potassium tungstate. A tenfold dilution of this solution in 0.9 M hydrochloric acid was used as a stock solution. Analyses were made by counting dried aliquots on platinum discs.

Potassium perrhenate was obtained from A. D. Melevan, University of Tennessee. This material, 99.9% pure, as indicated by spectrographic analysis, was used in determining the distribution coefficients of rhenium in hydrochloric acid. Aliquots for analysis containing 25-100 micrograms of rhenium were evaporated to dryness, taken up in one milliliter of 4.0 M perchloric acid and run on a polarograph. Preliminary studies had shown this analysis to be reliable and not critically dependent on the concentration of perchloric acid. A mixture of the tracers Re^{183} and Re^{184} was used for the determination of the distribution coefficients in nitric acid and for the column separation for tungsten. This material, obtained from J. O. Rasmussen of this laboratory, had been prepared by an alpha particle bombardment of tantalum in the 60-inch cyclotron and was electroplated on a platinum wire cathode. It was dissolved from the wire in a few drops of

concentrated nitric acid, heated to near dryness to oxidize to perrhenic acid and taken up in 1.0 M hydrochloric acid, or in 1.0 M nitric acid for the equilibrations in nitric acid. Analyses were made by counting suitable aliquots evaporated on platinum discs.

Distribution Coefficients. Between 2 and 50 mg. of resin were mixed with 2-50 ml of solution for at least 15 hours at 25°, though equilibrium was apparently attained in not over two hours for all four elements. These weights and volumes were chosen so that the distribution between resin and solution was approximately equal, in order to obtain maximum accuracy in the determination of the coefficient. This sometimes required preliminary trials to find approximate values. The solutions were prepared by adding aliquots of stock solutions to measured volumes of hydrochloric or nitric acid of known concentration. The final acid concentration was generally determined from these dilutions but was sometimes checked by an analysis of the solution after equilibration with resin. In no case was the foreign ion concentration, such as that of sodium from the sodium molybdate, over 0.001 molar. Aliquots of solution were analyzed after equilibration, and the amount of element adsorbed on the resin was determined by difference.

Separations. The optimum concentrations of hydrochloric acid for the separations were chosen from the results found for the distribution coefficients. Molybdenum and technetium in 0.5 ml of 1.0 M hydrochloric acid were added to a column of resin 3 mm in diameter and 21 mm in length. When the levels of liquid had just reached the top of the resin, elution was continued with 1.0 M hydrochloric acid, at the rate of 1 ml in 15 minutes, to remove molybdenum. Technetium was then removed from the column with 4.0 M nitric acid at the same rate of elution. Similarly, tungsten and rhenium in

1 ml of 1.5 M hydrochloric acid were added to a column 4 mm in diameter and 50 mm in length and the tungsten was eluted with the same acid. Rhenium was then eluted with 4.0 M nitric acid.

RESULTS

The distribution coefficient is defined by the equation:

$$K_D = \frac{M_r \times \text{ml solution}}{M_\ell \times \text{g resin}}$$

where M_r and M_ℓ are the fractions of the measured element in the resin and liquid phases, respectively. The dependence of K_D on the concentration of hydrochloric acid for the four elements is shown in Figure 1, and the dependence on the concentration of nitric acid, for technetium and rhenium, is shown in Figure 2. The curves for molybdenum and rhenium in hydrochloric acid are similar to those of Meloche and Preuss,[2] who used Amberlite IRA-400 instead of Dowex-1, but the K_D values are about double their values. The present results indicate that the best separation of molybdenum and technetium should occur in about 1.0 M hydrochloric acid and the best separation of tungsten and rhenium in about 1.5 M hydrochloric acid.

Figure 3 gives the results of separating molybdenum and technetium in about the optimum concentration of hydrochloric acid, followed by the elution of technetium in 4.0 M nitric acid. The total molybdenum recovered in the first 4.0 ml of hydrochloric acid was 100% of the amount used and the recovery of technetium in the first 4.4 ml of nitric acid was 98%. For some reason 0.1% of the technetium activity appeared in the first milliliter of hydrochloric acid with the molybdenum, but no more appeared in the next 7 ml. To investigate the possibility that a foreign activity gave this result the technetium was recovered from the nitric acid eluant, and the

separation was repeated. Again, 0.1% of the technetium activity appeared in the first milliliter of hydrochloric acid; any impurity should have been removed in the first run.

The results of separating tungsten and rhenium are shown in Figure 4. A recovery of 101% of the tungsten was found in the first 6.0 ml of 1.5 M hydrochloric acid and a recovery of 93% of the rhenium was found in the first 8 ml of 4.0 M nitric acid. A longer column was used for this separation than for molybdenum and technetium because of the lower K_D values for this pair of elements.

The distribution coefficients previously obtained in perchloric acid for rhenium[2] indicate that this eluant would be better than nitric acid for the recovery of rhenium, and probably for technetium. When attempts were made to fume perchloric acid from counting plates, however, about half of the rhenium or technetium activity was lost. A readily volatile eluant is needed for easy recovery.

ACKNOWLEDGMENT

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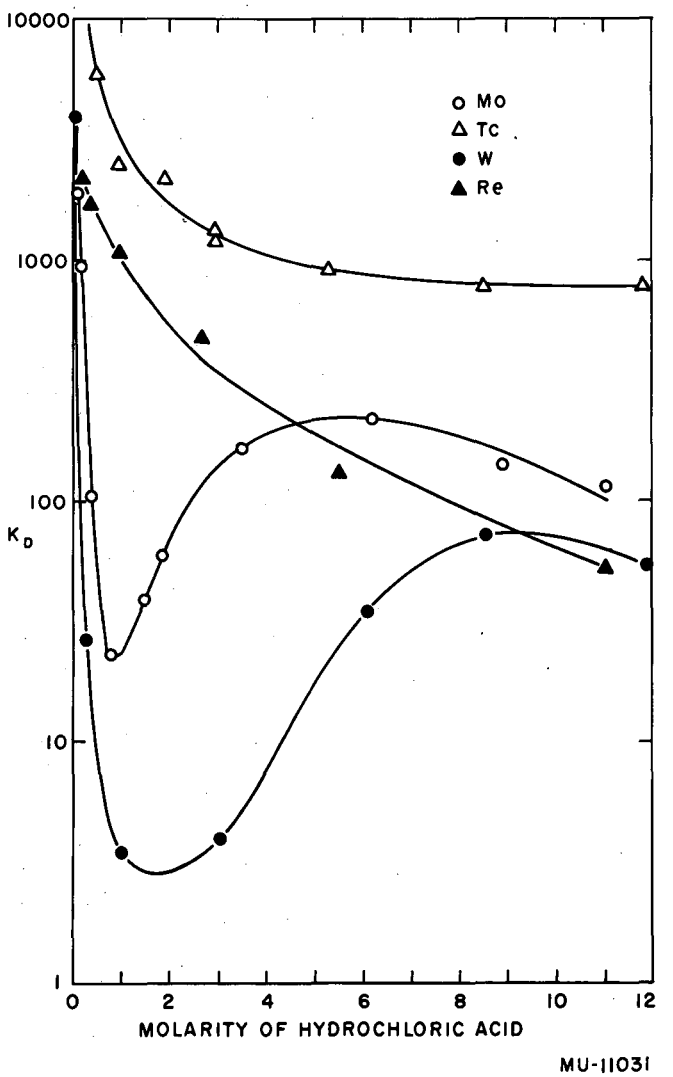

Fig. 1 Dependence of the distribution coefficient at 25° on the hydrochloric acid concentration with Dowex-1.

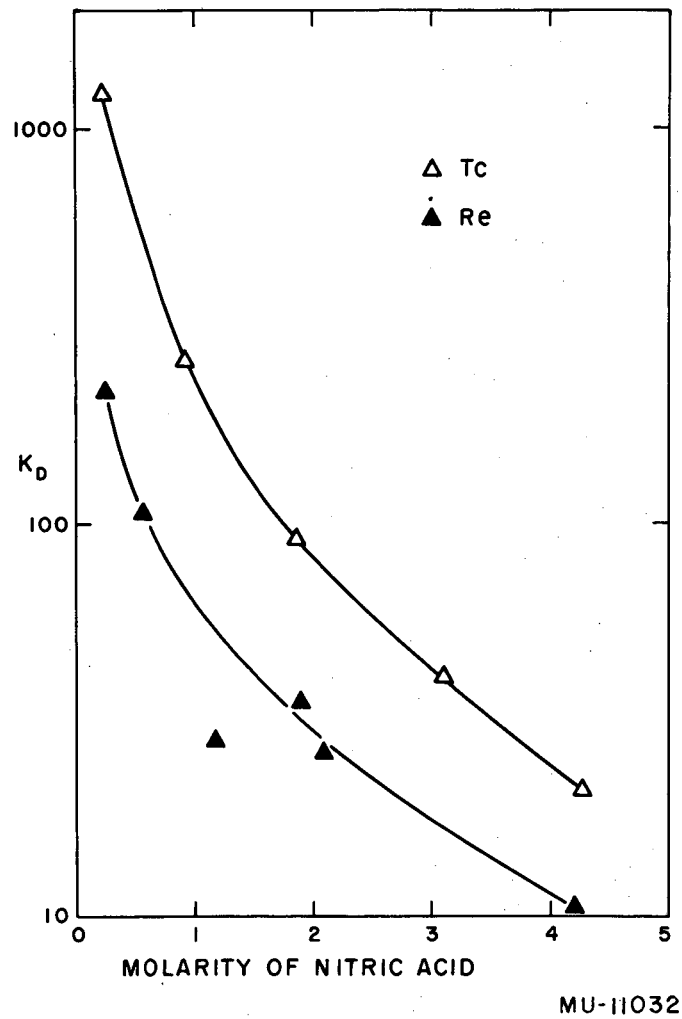

Fig. 2 Dependence of the distribution coefficient at 25° on the nitric acid concentration with Dowex-1.

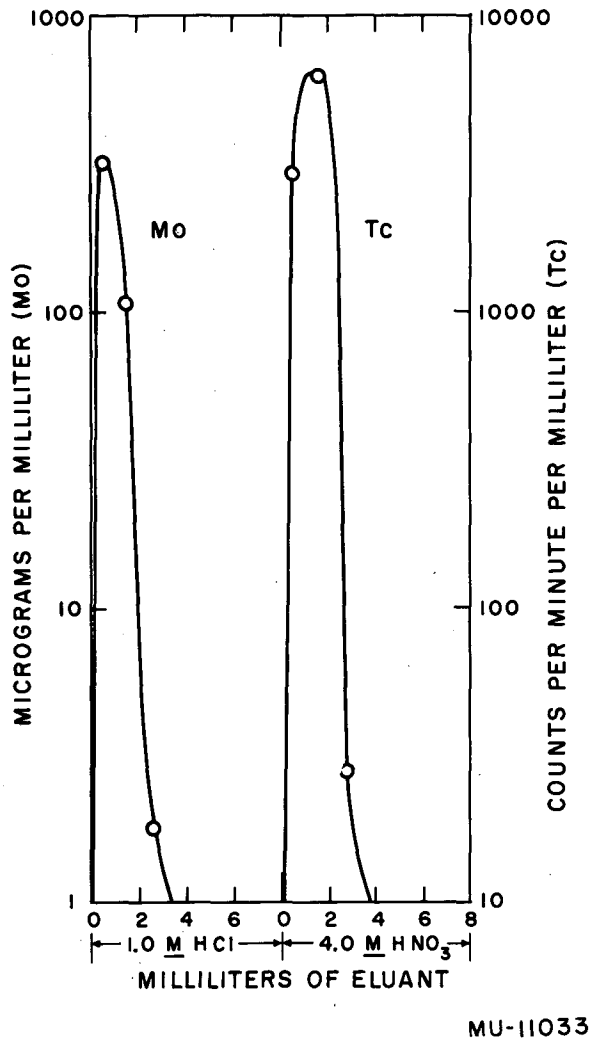

Fig. 3 Separation of molybdenum and technetium on Dowex-1; column 3 mm x 21 mm.

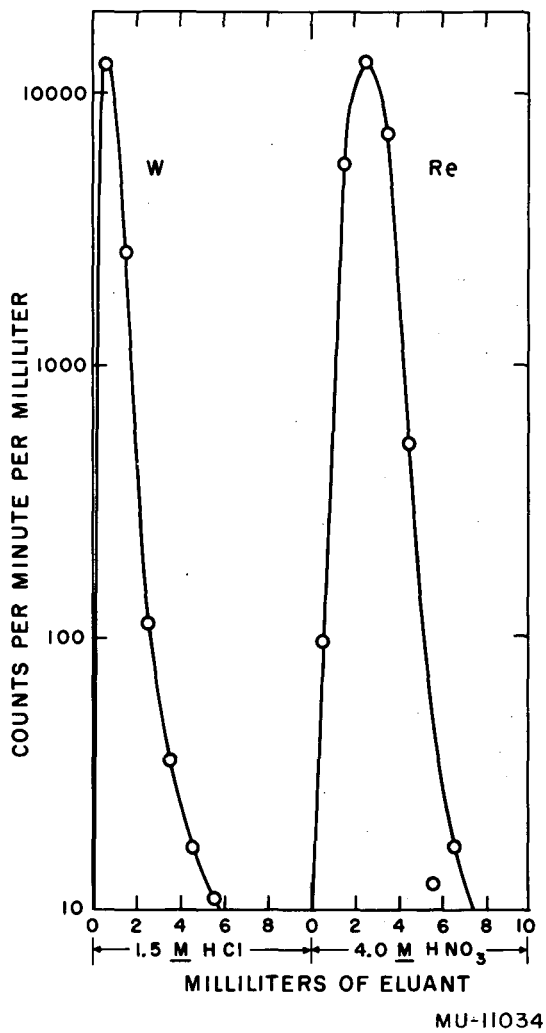

Fig. 4 Separation of tungsten and rhenium on Dowex-1; column 4 mm x 50 mm.