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January 27, 1950

THE SEPARATION OF TRACE AMOUNTS OF RADIOACTIVE Cs FROM MACRO QUANTITIES OF SODIUM AND POTASSIUM SALTS

INTRODUCTION:

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Recent attempts to separate fission products from urine salts in a form suitable for measurement by beta counting have involved the use of ion exchange resins to remove the ions present in macro quantities leaving the trace elements behind as a "thin" sample for counting techniques. The separation of Cs from Na and K was chosen as the starting point because of the relative difficulty of separating these elements with ordinary chemical techniques.

The results obtained on the preliminary work with solutions containing only the elements in question were deemed of sufficient interest to warrant reporting separately. Other difficulties from interfering ions in urine are now being studied.

SUMMARY:

A method for the separation of cesium from macro quantities of sodium and potassium using an ion exchange resin, Dowex 50, has been developed. A 95% recovery of cesium with a reduction of the solid content of 95% was found possible.

Curves illustrating the effect of acidity, column length, and flow rate are presented in the report. The sodium form, hydrogen form and ammonium form of Dowex 50 were investigated; the hydrogen form was found to give the best separation.

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cm. in diameter and 25 cm. long, partially filled with resin. The resin bed, the depth of which varied according to the experiment, was supported on a glass wool plug. A separatory funnel was connected to the top of the column to allow gravity feed, and the flow rate through the column was controlled by means of a stopcock connected to the bottom.

All work was done with a high capacity resin, Dowex 50. The resin was dry-screened and that portion between 50 and 60 mesh used for experimentation. After screening, the resin was converted to the H⁺ form by slurring it in 4N HCl for several hours. This acid slurry was poured into a column and the resin allowed to settle as the acid flowed from the column. The resin bed was then back-washed exhaustively with water to remove the excess hydrochloric acid. The sodium form and the ammonium form were made in the same manner using about 4 N sodium hydroxide or ammonium chloride on the acid form of the resin.

Solutions of cesium, sodium and potassium at the desired acidity, were then poured through the column at the chosen flow rate. After the feed solution had been exhausted, elution was carried on with acid at the same normality and flow rate as the feed.

A column of 40-60 mesh Dowex 50, 1 cm. in diameter and 10 cm. long with a flow rate of 0.7 cc/min/cm² of resin bed was used to study the effect of changing acidity. The feed solution was made with 30,000 dis/min of practically carrier-free Cs¹³⁷*, 0.5 gms. of sodium sulfate, and 0.5 gms. of potassium phosphate dissolved in 25 ml. of HNO₃ at the desired acid normality. The acidities for this study were varied in steps of 0.25 N from 0.25 N to 3.25 N HNO₃ with an additional measurement at 0.10 N HNO₃. The effect of flow rate was studied with the same type of column noted above using 0.25 N HNO₃ feed and elutriant with variations in the

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flow rate from 0.4 cc/cm² to 1.6 cc/cm². The effect of column length was studied with columns 5, 10, 15, and 20 cm. long, using a 0.25 N HNO₃ feed and elutriant.

The elutriate was sampled continuously. Each succeeding five ml. portion was evaporated to dryness on a tared stainless steel counting plate, the salts weighed and the sample counted for activity. The results were then plotted as weight versus volume through the column and as activity versus volume through the column. By this type of plot, the position of the slug or band containing the Cs fraction could be directly compared to the position of the band containing the Na and K salts. The volume between and the width of these bands could also be accurately determined.

Samples were counted on mica window Geiger counters with samples 0.191 inches from the tube face. All samples were counted on the same counter and mounted in the same manner so that true relative values could be obtained. As a result, none of the values are corrected for backscatter, self-absorption, etc.

RESULTS:

Figure I presents a typical elution curve obtained with the hydrogen form of the resin and eluted with 0.25 normal nitric acid followed by a 2 N nitric acid wash to remove the cesium. A summation of the effect of varying the acidity of the elutriant is given in Figure 2 where the width of the bands and the distance between the peaks, expressed as volume of elutriant, are plotted against the acidity. In preparing Fig. 2, all aliquots which weighed less than 10% (10 milligrams) or counted less than 3% (100 c/m) have been excluded to avoid plotting the tails of the bands. This data indicates a marked increase in the separations between the peaks below about 1 N acid. The width of the cesium band increased fairly rapidly at lower acidities but the width of the sodium and potassium bands remains relatively constant. Thus, it is possible to elute the sodium and potassium salts at low acidities with a small amount of elutriant and after removal of these salts to

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elute the carrier-free cesium with a small amount of strong acid as has been illustrated in Figure 1. From this data, it would seem that about 0.25 N elutriant will give a good separation with a permissible volume of wash. With lower acidities, the elution requires a large volume of wash to move the bands down the column and the separation for practical purposes is not better. At higher normalities the bands are much narrower but the separation is less efficient due to a relatively rapid increase in elution rate of the cesium fraction. This is illustrated by Figure 3 which is an elution curve with a 1.5 N wash. This curve may be contrasted to Figure 1. It should be noted that elution rate for all three elements increased with increasing acidities.

Figure 4 illustrates the effect of varying the length of the column. This is a plot of the width of the various bands and the distance between the peaks on the elution curves plotted against the length of the column. The distance between the peaks increases as would be expected, with an increase in column length. However, the width of the bands also increase slightly resulting in an overlapping of the tail of the two bands with only a slight increase in the yield of pure product.

Figure 5 presents the data obtained on the effect of changing flow rate on the separation. Apparently, a change in the flow rate in this range has very little effect on the separation. Reproducibility of this work as determined by five similar runs indicated a variation of about ± 10 ml. for band width and location. Thus, the slight hump noted in the curve of Figure 5 is probably not significant.

The sodium form and the ammonium form of Dowex 50, did not give as good a separation as the hydrogen form. The distance between peaks was smaller, which resulted in a poor separation. The sodium form did give a very narrow sodium-potassium band overlapped by the cesium band and it is possible that a longer column would give good separations.

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The optimum procedure, evolved from these studies, uses a column of Dowex 50, 1 by 10 cms., with a flow rate of 0.75 ml/min/cm^2 of resin bed. The samples, containing one to 2 gms. of salts are diluted to 20 ml. and the acidity adjusted with nitric acid to 0.25 N. The sample is allowed to flow through the column followed by 100 mls. of 0.25 N nitric acid. The elutriant from these steps is discarded, and the column washed with 60 ml. of 2 N nitric acid to elute the cesium rapidly. The column is then regenerated for reuse by backwashing with 400 to 500 ml. of 4 N nitric acid and rinsing with water.

This method gives about a 95% reduction in the amount of sodium and potassium salts with 90-100% yields on the cesium. The reproducibility of the amount of cesium recovered is about $\pm 5\%$. The exact recovery is somewhat doubtful because of the factors involved in counting the amount of cesium introduced into the column and the amount removed. The yield, as determined by a direct count of an evaporated aliquot of the carrier-free spike solution was 105 to 110%. The yield based on the amount recovered in the cesium fraction divided by the total activity recovered from the column is 85 to 90%. The low yields, in the latter case, are due to the presence of K^{40} which will add to the total amount recovered from the column when measured by beta counting techniques. The high yields, in the former case, are due to a distribution of the evaporated aliquot of feed solution on the counting plate that gives a lower counting geometry. Radioautographs of these plates showed that most of the activity had spread to the outside of the plate, thus resulting in a lower counting rate. The small amount of salts associated with the elutriate from the column appeared to hold the radioactive cesium evenly distributed over the plate resulting in counting rates higher than those of the standards produced from the aliquots. The average counting rate of a series of ten plates prepared with 10 milligrams of sodium phosphate per plate and a known amount of cesium spike,

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was compared to the counting rate of 10 plates with an equal amount of cesium spike but no holding agent. The counting rate of the plates with the holding agent averaged 10% higher than those without, indicating a 95 to 100% yield for the experiment.

DISCUSSION:

The purpose of these experiments was to devise, in the shortest possible time, a method of separating radioactive cesium from macro quantities of sodium and potassium. This industrial development did not allow a methodical search for more optimum conditions or for an explanation of the theoretical implication of the results obtained. The effect of temperature, resin size, optimum column length and other minor variables are still to be investigated. The effects of a specific cesium complexing agent, such as bismuth nitrate should also be investigated. It will be noted that the bismuth would later have to be removed by a sulfide precipitation or perhaps by careful elution. However, the results of this study have established a practical method for the desired separation.

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FIGURE I
Separation of Cs from K & Na by
Ion Exchange at 0.25 N
Column: 1 x 10 cm. H + form Dowex-50
Flow = 1 ml/min/cm²
Wash = 0.25N for 125 ml.
= 2.0N for 40 ml.

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FIGURE 2

Effect of Acidity on the Separation of Trace Amounts of Cs
from Na_2SO_4 & K_3PO_4

Column Conditions

Resin - H form Dowex-50

Size of Bed - 1×10 cm.

Flow Rate - 1 ML/min/cm^2

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FIGURE 3
Separation of Cs from
K & Na by Ion Exchange
at 1.50 N

Column: 1x10 cm. H+
form Dowex-50

Flow = 1 ml/min/cm²

Wash = 1.50 N

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FIGURE 4

Effect of Column Length on Separation of Cs from Na & K
 Column = 1 cm. diam. H+ form Dowex - 50 Flow = 1 cm/min/cm²
 Normality of Eluant = 2.0

FIGURE 5

Effect of Flow Rate on Separation of Cs from Na & K

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