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A New Type of Ion-exchange Column for the Separation of Radioactive Bromine or Chlorine

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The radioactive isotopes of chlorine and bromine — ^{36}Cl and ^{82}Br — usually are prepared through (n, γ)-reactions in the uranium reactor. In order to increase the specific activity the use of a Szilard-Chalmers reaction is desirable. As the target material for the irradiation in such a case is a halate and the radioactive isotope appears as halide, the chemical problem associated with the Szilard-Chalmers reaction is the separation of halide from halate. This problem has been treated before by the present author [1] but the methods used cannot be applied to preparations, the radioactivity of which is so high, as to make necessary remote control technique.

The purpose of this investigation is to develop a suitable method which may be used for the separation of highly radioactive bromide or chloride, from bromate respectively chlorate. The best method is now considered to consist in the use of an ion-exchange column, since such an apparatus may be easily run by remote control.

THE CHOICE OF ION-EXCHANGER

The separation of halide and halate must take place in neutral or alkaline solution since an isotopic exchange takes place in acid solution. The only existing ion-exchange resin which may well be used for such solutions is Amberlite IRA-400. Some preliminary experiments showed, however, that it was very difficult to get this product absolutely free from chloride. Thus a small column was treated for several days with 20 % sodium hydroxide with a flow rate of about 0.3 mls per minute per cm^2 without getting the eluate

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free from chloride. Since it is essential to produce a pure product, the possibility of the preparation of a new type of ion-exchanger was considered.

The following considerations led to the development of the material. If a silver compound, the solubility of which is larger than that of silverbromide, is treated with a solution containing bromide, part of the anion in the compound is replaced by bromide:

$$AgY + Br^- \rightleftharpoons AgBr + Y^- \tag{1}$$

where Y is some anion. The equilibrium between the solution and the solid phase is determined by

$$\frac{\{Y^-\} \cdot \{AgBr\}}{\{AgY\} \cdot \{Br^-\}} = K \tag{2}$$

where $\{\ \}$ denotes activities. Furthermore it is true that

$$\frac{\{Ag^+\} \cdot Br^-\}}{\{AgBr\}} = K_1 \tag{3}$$

and

$$\frac{\{Ag^+\} \cdot \{Y^-\}}{\{AgY\}} = K_2 \tag{4}$$

If AgBr and AgY form ideal solid solutions, K_1 and K_2 equals the solubility products L_{AgBr} and L_{AgY}. Hence

$$K = \frac{L_{AgY}}{L_{AgBr}} \tag{5}$$

If AgY and AgBr do not form solid solutions, AgY is completely converted into AgBr if Br^- is present in excess, and the solubility product of AgY is larger than that of AgBr. Accordingly an adsorption column containing a suitable silver compound could be used to remove bromide from a solution. It is desirable to use a compound which does not form solid solutions with silverbromide. If the solution contains bromate the solubility product of the compound used must be smaller than that of silverbromate. The best silver compound was considered to be silver oxide. In Table 1 is listed the concentration of silverion in saturated solutions of some silver compounds [2]. It is seen from the table that a column containing silver oxide will absorbe chloride and bromide but not bromate. Furthermore it is improbable that silver oxide will form mixed crystals with either of the other compounds.

Table 1. Silverion concentration in saturated solutions of different silver compounds.

Compound	$[Ag^+]$
$AgBrO_3$	$6.7 \cdot 10^{-3}$
Ag_2O	$1.85 \cdot 10^{-4}$
AgCl	$1.05 \cdot 10^{-5}$
AgBr	$4.7 \cdot 10^{-7}$

If silver oxide is present as large aggregates the establishment of equilibrium between the solution and the solid phase must be expected to be a very slow process. Probably only the surface will react at once and after absorption of bromide during a longer time when perhaps deeper layers are converted to bromide it would be difficult to desorbe the bromide. It should thus be convenient to have the silver oxide present in very thin layers adsorbed on some inert material having a large surface area. Diatomaceous earth was believed to be a suitable adsorbens for the silver oxide.

Accordingly silver oxide adsorbed as a thin layer on diatomaceous earth constitutes an ion-exchanger capable of exchanging chloride or bromide against hydroxyl ions. Once the chloride or bromide is adsorbed on a column containing the ion-exchanger and thus separated from the bulk of the solution it may be eluted with a solution of sodium iodide.

EXPERIMENTAL

Preparation of ion-exchanger: 5 ml of 0.1 *M* silver nitrate solution were added to different amounts of diatomaceous earth suspended in water. Then a slight excess of 0.1 *M* NaOH was slowly added during vigorous stirring. It was found that 5 g of diatomaceous earth had to be used to completely adsorbe the silver oxide formed. If smaller amounts were used two solid phases appeared, one consisting of pure silver oxide not adsorbed. If, however, 5 g or more per 5 ml of 0.1 *M* silver nitrate were used, a homogeneous, fine, brownish suspension was obtained, apparently consisting of silver oxide adsorbed as a very thin layer on the diatomaceous earth. The substance was washed by decanting with water containing a little sodium hydroxide.

Separation experiments: A column shown in Fig. 1 was used. The ion-exchanger was allowed to settle in the column filled with water. The solution to be treated was allowed to flow with a rate of 0.2—0.3 ml per minute.

Experiment 1: 5 ml of a 0.02 *M* solution of sodium bromide was poured into the column. It was found that a very sharp band of silver bromide about 5 cm long was formed. Then a 0.02 *M* solution of sodium iodide was poured into the column. It was found that the bromide band migrated down the column followed by an iodide band. The boundary between bromide and iodide was very sharp. However after some ml of sodium iodide solution had flowed, part of the silver iodide in the top of the column was colloidally dissolved and appeared in the eluate.

Experiment 2: The peptization of silver iodide ought to be prevented if the solution contains a positive ion of higher valence. Hence in this experiment the bromide and iodide solutions used were made 0.01 *M* in Ba^{2+}. It was found that in this case it was possible completely to elute the bromide with sodium iodide without the appearance of any colloidal silver iodide. As soon as the bromide band had reached the bottom of the column samples of 1—5 ml volume were taken from the eluate and bromide and iodide determined by potentiometric titration with silver nitrate. The results are shown in Fig. 2.

Experiment 3: 5 ml of a solution containing 50 g of potassium bromate per litre and being 0.02 *M* in sodium bromide were allowed to flow through the column. The bromide was eluted with a solution 0.01 *M* in sodium iodide and 0.01 *M* in Ba^{2+}. In the eluate bromate was determined by reduction to Br_2 with Br^- followed by colometric determination of Br_2. Bromide and iodide were determined by potentiometric titration with silver nitrate. The results are shown in Fig. 3.

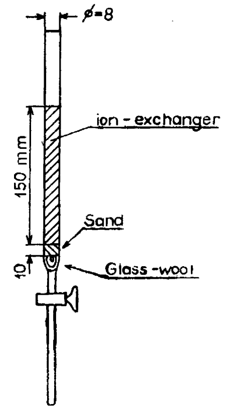

Fig. 1. Ion-exchange column.

Experiment 4: The bromide preparations obtained from the column contain Ba^{2+} and Ag^+. In order to get a pure solution a 4 cm layer of a cation exchanger — Amberlite IR-120 —in hydrogen form was placed under the anion exchanger in the column. This experiment was performed in order to study the boundary between iodide and bromide in this case. In order to simplify the analytical determinations radioactive bromine — ^{82}Br- and iodine — ^{131}J — were used. The experiment was performed according to experiment 3, the only difference being that bromide and iodine were determined by radioactivity measurements and that 9 ml of bromide solutions were used. Thus samples from the eluate were prepared by neutralizing with sodium hydroxide followed by evaporation of 0.05 ml on glass disks. The radioactivity of the samples was measured with a scale-of-64 amplifier using an end-window counter. Two measurements were carried out, one of which was performed 14 days after the end of the experiment when ^{82}Br had decayed completely. From the activity at the last measurement the iodine concentration could be

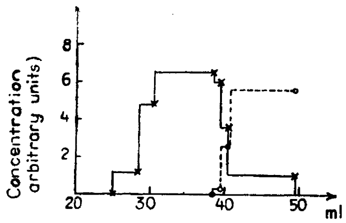

Fig. 2. Experiment 2. Elution curves.

× *bromide* ○ *iodide*

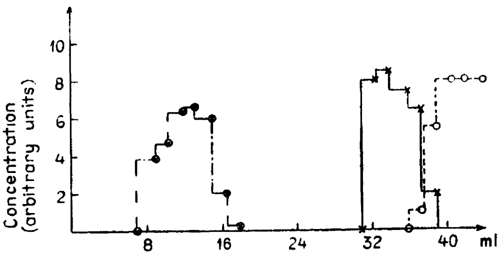

Fig. 3. Experiment 3. Elution curves.

● *bromate* × *bromide* ○ *iodide*

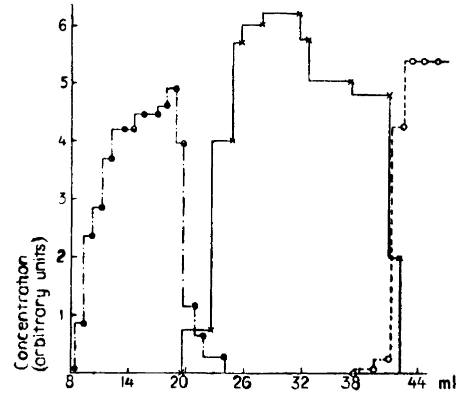

Fig. 4. Experiment 5. Elution curves.
⊕ *bromate* × *bromide* ○ *iodide*

determined and from the first measurement the sum of iodide and bromide concentrations could be obtained. The results are shown in Fig. 4.

Experiment 5: This experiment was performed in order to make sure that separation of perchlorate and chloride could be carried out with the ion-exchanger used. 5 ml of a solution 0.1 M in sodium perchlorate and 0.02 M in sodium chloride were used. The elution was carried out with a solution 0.02 M in sodium iodide. Both of the solutions were 0.01 M in Ba^{2+}. It was found that the column behaved exactly as in the cases with bromide and bromate.

DISCUSSION

The experiments have shown that the ion-exchanger prepared may be successfully used to separate small amounts of bromide or chloride from alkaline solutions containing ions which prevent the formation of colloidal silver halide solutions. From the elution curves shown it is seen that the boundary between the bromide and the iodide is not absolutely sharp. The yield of bromide free from iodide was about 90 %. This surely is due to the fact that the solution has to move a rather long distance after the ion-exchanger. For preparative purposes it is desirable to increase the yield. This ought to be possible through a better shaping of the column. A following paper on the preparation of ^{82}Br will deal more closely with this problem.

The capacity of the ion-exchanger has been found to be $4 \cdot 10^{-5}$ equivalents per cm^3 bed wolume. Since the calculated capacity of dry substance is 10^{-4} equivalents per gram the liquid content of the column is approximately 60 vol-% if the density is set equal to one. Some simple batch experiments have shown that the establishment of equilibrium between solution and ion-exchanger is practically instantaneous. Hence the column may be easily calculated for the solution to be separated. In order to get only a small part of the bromide in the iodide containing fraction of the eluate, the diameter of the column has to be such that the bromide band will be at least 5 cms long. As mentioned above in this case 90 % of the bromide may be obtained free from iodide.

For the calculation of the column the following notations are used:

Volume of solution = V cm^3
Capacity of ion-exchanger = C mequiv./cm^3
Volume fraction of liquid in the column = α
Area of the column = A cm^2
Depth of ion-exchanger = l cm

The area of the column is obtained from the equation:

$$V \cdot [\mathrm{Br}^-] \geqq 5A \ (c + \alpha[\mathrm{I}^-]) \tag{6}$$

The depth of the ion-exchanger is determined by the length of the bromide band and the iodide concentration of the solution used for the elution. The rest of the original solution which is in the column when the addition of iodide solution is started must be displaced before the bromide band reaches the lower end of the exchanger bed. This gives the equation:

$$\frac{V \cdot [\mathrm{Br}^-]}{A(c + \alpha[\mathrm{I}^-])} + \frac{\alpha \cdot A \cdot l \cdot [\mathrm{I}^-]}{A(c + \alpha[\mathrm{I}^-])} = l \tag{7}$$

Hence

$$l = \frac{V \cdot [\mathrm{Br}^-]}{C \cdot A} \tag{8}$$

As the bromate concentration owing to diffusion in the solution does not fall sharply, it is advisable to make the depth about double the value obtained from equation (8).

Using the above mentioned values for α and C, the values for A and l may be calculated from (6) and (8).

SUMMARY

An anion-exchanger consisting of silveroxide adsorbed on diatomaceous earth has been prepared.

It has been demonstrated that this substance may be used to separate small amounts of bromide or chloride for preparative purposes.

Equations for the calculation of the adsorption column have been derived.

LITERATURE

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