S 71. *The Separation of* ^{82}Br *from Neutron-irradiated Sodium Bromate.*

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Methods for the preparation of ^{82}Br by Szilard–Chalmers reaction with sodium bromate have been devised. Different methods have been used to deal with small or large amounts of sodium bromate. If large amounts are involved, a two-step separation is accomplished; the first step involves a separation by use of a non-isotopic carrier, and the activity is then separated from this by use of a very small amount of inactive bromide as carrier. Various carriers have been used for the first step and different methods for the separation in the second step have been studied.

If a (n, γ)-reaction is used for the preparation of ^{82}Br the separation of the radioactive nuclide by a Szilard–Chalmers reaction is necessary. The two possible kinds of target-compounds for the irradiation are the organic bromides and the bromates (Szilard and Chalmers, *Nature*, 1934, **134**, 462; Lu and Sugden, *J.*, 1939, 1273; Amaldi, *et al.*, *Proc. Roy. Soc.*, 1935, *A*, **149**, 538; Libby, *J. Amer. Chem. Soc.*, 1930, **62**, 1940). The Szilard–Chalmers reaction has been investigated for organic bromides by many authors, and methods have been given for the preparation of ^{82}Br samples with a very good specific activity (Lu *et al.*, *loc. cit.*; Erbacher and Philipp, *Ber.*, 1936, **64**, 893). The retention of radiobromine in the organic phase, however, is often larger than 50% and in any case not smaller than 30%; and as it has been reported that the retention of sodium bromate is nearly zero (Amaldi *et al.*, *loc. cit.*; Libby, *loc. cit.*), it seemed worth while to elaborate a method for the use of this compound for the preparation of ^{82}Br. The nuclear reaction has as a consequence that the bromate ion is split and the radioactive bromine atoms appear as bromide ions (Libby, *loc. cit.*); thus the problem is to separate chemically tracer amounts of bromide ions from large amounts of bromate ions. The radioactive bromine is to be obtained in the form of sodium bromide.

From a chemical viewpoint the bromide ions could be oxidized to free bromine which may then be extracted with, *e.g.*, carbon tetrachloride. It would be possible to do this without the addition of any carrier. Unfortunately there is a thermal exchange between bromine and bromate ion, and therefore this method fails (Libby, *loc. cit.*). The chemical state of the activity must be that of bromide ion as long as bromate ions are present.

Experimental.

The irradiation of sodium bromate was carried out by a 350-millicurie radium–beryllium neutron source. The solid salt, together with the source, was placed in the centre of a cylindrical block of paraffin wax. All precipitates were filtered off in a filtering device with a horizontally-mounted filter paper. After being filtered off and washed with water the precipitates were treated with alcohol and then with ether and sucked dry.

For the measurement of the radioactivity a scale-of-64 Geiger–Müller counter was used. If the samples were measured the same day as the irradiation was finished, only the 18-minutes ^{80}Br in equilibrium with its isomeric 4·4-hours parent was measured. This was achieved by the use of a cylindrical Geiger–Müller tube with a wall thickness of about 200 μ. If the samples were measured after 24 hours or more, the 4·4-hours activity had practically disappeared and only the 34-hours activity of ^{82}Br was measured by a tube with a thin mica window. For this method of measuring the correction of the activity for disintegration is simpler. All measurements of the 4·4-hours activity were carried out at least 2 hours after the last chemical operation, in order to avoid any effect of the isomeric transition. In every experiment the content of radioactive bromine present as bromide ions in solution was determined in the following way: 100 mg. of sodium bromide were added, after which the bromide ions were precipitated by an equivalent amount of silver nitrate; the silver bromide was filtered off and measured in the counter.

In most of the experiments a solution of 10 g. of irradiated sodium bromate in 50 ml. of water was prepared. We shall refer to such a solution as " solution A."

Before irradiation the sodium bromate used was purified by precipitation with silver nitrate. The precipitate containing any bromide ion impurities was filtered off and the filtrate further purified by recrystallisation.

Experiment 1.—1 Mg. of sodium bromide was added to 5 ml. of " solution A." The bromide ions were precipitated by an equivalent amount of silver nitrate, the solution was centrifuged, and the liquid decanted. The silver bromide was then stirred on the water-bath with 5 ml. of a solution containing an equivalent amount of sodium iodide. The reaction was allowed to proceed during 10 minutes. The precipitate was filtered off and washed twice with 10 ml. of hot water. The activity of the filtrate was 300 counts/min.; that of 5 ml. of " solution A " was 305.

Experiment 2.—100 Mg. of sodium chloride were added to 5 ml. of " solution A." Silver chloride was precipitated by an equivalent amount of silver nitrate. The activity of the silver chloride was 460 and that of 5 ml. of " solution A" was 455 counts/min.

Experiment 3.—100 Mg. of sodium iodide were added to 5 ml. of " solution A." Silver iodide was precipitated by an equivalent amount of silver nitrate. The activity of the silver iodide was 388, and that of 5 ml. of " solution A " was 390 counts/min.

Experiment 4.—Different amounts of N-silver nitrate were added to 5 ml. of " solution A " as indicated in the table. The activity of the precipitated silver bromate was measured. The activity of 5 ml. of " solution A " was 290 counts/min.

$AgNO_3$, ml.	Method of addition.	Activity, counts/min.
0·5	Drop by drop with vigorous stirring	300
1·5		284
0·2	The whole portion at once without stirring	280
0·5		298

Experiment 5.—About 70 mg. of silver chloride were prepared by addition of silver nitrate to a 0·1N-solution of sodium chloride. The silver chloride was filtered off, washed with water, and was not allowed to dry. Then 5 ml. of " solution A " were filtered through the silver chloride. The activity of the silver chloride was 366 and that of 5 ml. of " solution A " was 372 counts/min.

Experiment 6.—About 120 mg. of silver iodide were prepared in the same way as was the silver chloride in experiment 5. 5 Ml. of " solution A " were filtered through the silver iodide. The activity of the silver iodide and that of 5 ml. of " solution A " were 410 counts/min.

Experiment 7.—About 100 mg. of silver bromate were precipitated by addition of N-silver nitrate to a saturated solution of sodium bromate. The precipitate was filtered off and washed with water. 5 Ml. of " solution A " were filtered through the silver bromate. The activity of the silver bromate was 264 and that of 5 ml. of " solution A " 295 counts/min.

Experiment 8.—To 5 ml. of " solution A " were added different amounts of sodium bromide. The solutions were filtered through silver iodide, and the retention of radiobromine in the solution was determined. The results are shown in Fig. 1.

Experiment 9.—5 Ml. of " solution A " were filtered through 120 mg. of silver iodide. Then the silver iodide was stirred on a boiling water-bath with a solution of 1 mg. of sodium bromide in 15 ml. of water. The activity of the solution is plotted against the time of reaction (Fig. 2).

Experiment 10.—80 G. of irradiated sodium bromate were dissolved in 175 ml. of water. The solution was filtered through 120 mg. of silver iodide, and the activity of the filtrate determined in fractions each of 25 ml. The retention was calculated for each fraction (see Fig. 3).

FIG. 1.

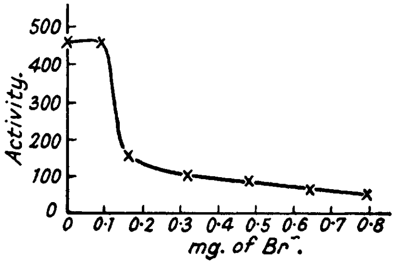


FIG. 2.

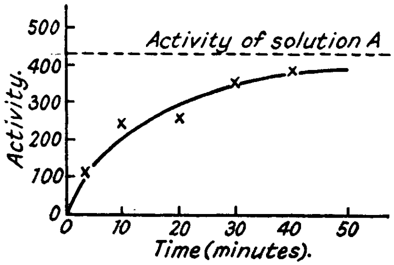
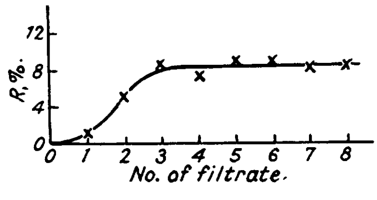


FIG. 3.



DISCUSSION.

If only small amounts of sodium bromate are to be treated, the separation is simple. The activity is precipitated with a small amount of inactive silver bromide as carrier. In order to transform the radioactive bromine into sodium bromide the precipitate is treated with an equivalent amount of sodium iodide. With one mg. of silver bromide the reaction $AgBr + NaI \rightarrow AgI + NaBr$ is complete in about 10 minutes at 100°.

If large amounts of sodium bromate are to be treated, the amount of carrier bromide has to be larger and no high specific activity can be obtained. In this case it seems better first to separate the radiobromine from the sodium bromate solution, using a carrier which may then be separated from the final product. The amount of carrier may be chosen so as to make convenient handling possible.

According to experiments 2 and 3, bromide ions may be completely co-precipitated with silver chloride or silver iodide. This is in accordance with common rules. Further, experiment 4 shows that silver bromate also may serve as carrier for tracer amounts of bromide ions. The experiment shows that the co-precipitation is complete, irrespective of the method of precipitation.

It is, however, not necessary to carry out a precipitation in the solution. The radioactive bromide ions may be adsorbed on sparingly soluble silver salts, and a filtration through a layer of silver chloride or silver iodide removes the whole of the activity from the solution. According to experiment 7, 90% of the activity is adsorbed on silver bromate.

The separation of radiobromine from the carrier may be effected in different ways. If silver chloride or silver bromate is used, the precipitate is dissolved in as small an amount of dilute aqueous ammonia as possible. To this solution is added some sodium bromide, the amount of which may be as small as 0·1 mg. The silver bromide precipitate thus formed, containing the whole of the activity, is centrifuged off and then treated with an equivalent amount of sodium iodide as in experiment 1.

If silver iodide is used as carrier, this method fails and the separation must be carried out by an exchange reaction :

$$Br^* (AgI) + Br^- \rightleftharpoons Br (AgI) + Br^{*-} \qquad (2)$$

At equilibrium

$$[Br^{*-}]/[Br^* (AgI)] = [Br^-]/[Br (AgI)] \qquad (3)$$

and hence the success of this method depends on the maximum amount of bromide ions which can be adsorbed on the amount of silver iodide used. If [Br (AgI)] is large, $[Br^-]$ must be large in order to get most of the activity in the solution, but this means that a large amount of inactive bromide ions must be added. This must of course be avoided if a high specific activity is to be obtained. To determine the maximum amount of silver iodide which can be adsorbed, experiment 8 was performed. It is seen from Fig. 1 that about 0·1 mg. is adsorbed on 120 mg. of silver iodide. Under these circumstances, according to equation (3), 90% of the activity is transferred to the solution by exchange if the amount of bromide ions present is 1 mg., an amount which may be permitted.

The kinetics of the exchange reaction have been approximately determined. According to experiment 9, about 50 minutes are needed for almost complete exchange. The results, of course, are valid only when radiobromide is adsorbed on silver iodide and not if precipitated. In such a case the exchange reaction certainly is determined by the rate of diffusion of bromide ions in silver iodide, a process which may be expected to be very slow.

In order to make sure that the adsorbing power of silver iodide is not decreased during treatment with large amounts of sodium bromate solution, experiment 10 was performed. The results shown in Fig. 3 are interpreted as follows. Before the addition of the first portion of sodium bromate solution the silver iodide forms a uniform layer on the filter paper. As the filtration proceeds the silver iodide fairly soon forms bigger aggregates which do not occupy the whole of the filter paper. Hence part of the solution may pass through the filtering device without touching the silver iodide, and as the rate of flow is rather high the bromide ions of the part of the solution which does not touch the silver iodide cannot diffuse to its surface and consequently are not adsorbed. Hence, the retention of about 8% is not caused by a decrease in adsorbing power but is a consequence of the practical difficulties of the filtration. In order to avoid these it is better to use a thicker layer of silver iodide obtained by diminishing its diameter. The diameter of the adsorbing layer was 35 mm. in this experiment. It is advisable to make it about 20 mm.

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