CONCENTRATION OF BROMIDE IONS IN SEAWATER BY ISOTOPIC EXCHANGE WITH MERCURIOUS BROMIDE

By
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6 JUNE 1972

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In a previous study it was reported that silver bromide can concentrate the radioactive bromide ions in seawater by a process of isotopic exchange. Mercourous bromide looked more favorable because of its lower solubility and lower cost and it was thus used to determine its effectiveness, relative to silver bromide, in concentrating bromide ions from seawater. The effect of the height of the mercourous bed, flow rate and volume (residence time) of the seawater on the amount of bromide ions exchanged was studied. Each of the variables was found to have a significant effect. The results indicated that under the same conditions mercourous bromide can concentrate the bromide ion in seawater slightly more than the silver bromide.
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<tr>
<td></td>
<td>ROLE</td>
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CONCENTRATION OF BROMIDE IONS IN SEAWATER
BY ISOTOPIC EXCHANGE WITH MERCUROUS BROMIDE

Prepared by:
Stephen C. Poti

ABSTRACT: In a previous study it was reported that silver bromide can concentrate the radioactive bromide ions in seawater by a process of isotopic exchange. Mercurous bromide looked more favorable because of its lower solubility and lower cost and it was thus used to determine its effectiveness, relative to silver bromide, in concentrating bromide ions from seawater. The effect of the height of the mercurous bed, flow rate and volume (residence time) of the seawater on the amount of bromide ions exchanged was studied. Each of the variables was found to have a significant effect. The results indicated that under the same conditions mercurous bromide can concentrate the bromide ion in seawater slightly more than the silver bromide.
Concentration Of Bromide Ions In Seawater By Isotopic Exchange With
Mercurous Bromide

There is a need for determining radioactive bromide ions in the ocean. The amount
of bromine in seawater is relatively small (65 mg/l), and a substantial improve-
ment in radioactive bromine detection sensitivity could be achieved by concentra-
tion of the bromine. A fast-reacting in-situ system is required for concentration
of the bromine from large volumes of seawater.

In a previous study it was reported that silver bromide can concentrate the
radioactive bromide ions in seawater by a process of isotopic exchange to permit
counting of any radioactive bromine atoms present. Mercurous bromide looked more
favorable than silver bromide because of its lower solubility and lower cost, and
it was used to determine its effectiveness, relative to silver bromide, in con-
centrating bromide ions from seawater. The results indicated that under the same
conditions mercurous bromide can concentrate the bromide ions slightly more than
the silver bromide.

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ROBERT WILLIAMSON II
Captain, USN
Commander

ALBERT LIGHTBODY
By direction
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INTRODUCTION

A method was required for the in-situ determination of radioactive bromide ions in seawater. The amount of radioactive bromide ions is expected to be very low and thus sensitive methods of analysis are sought. A substantial improvement in sensitivity could be achieved if the radioactive bromide ions in the seawater could be concentrated and then counted.

In a previous study\(^1\) it was reported that silver bromide, AgBr, can concentrate the bromide ions in seawater by a process of isotopic exchange and that the seawater can desorb the bromide ions from AgBr. Another compound, mercurous bromide, Hg\(_2\)Br\(_2\), looked more favorable because of its lower solubility and lower cost and was studied to determine its effectiveness, relative to AgBr, in concentrating bromide ions under similar conditions.

APPROACH

Seawater samples with \(^{82}\)Br activity were passed through a column that contained the isotopic exchanger, Hg\(_2\)Br\(_2\). The amount of \(^{82}\)Br exchanged was determined by gamma counting aliquots of the sample before and after passage through the Hg\(_2\)Br\(_2\) bed.

A 3 x 3 x 3 factorial experiment was set up to get a better study of the effect of the variables on the amount of \(^{82}\)Br exchanged. The factorial experiment is useful in determining whether or not variations due to factors studied are greater than might be expected from purely random variations, and also in determining whether or not interactions between pairs of factors are significant. The factors studied in this experiment were the following: (1) height of the Hg\(_2\)Br\(_2\) bed in the column, (2) flow-rate, and (3) volume (residence time, which is the time duration of flow).

In addition to the factorial experiment, the desorption rate of \(^{82}\)Br from Hg\(_2\)Br\(_2\) column was studied.

EXPERIMENTAL

MATERIALS

1. Mercurous bromide (Reliable Chemical Co.). The mercurous bromide was crushed and sieved through a Tyler standard screen. A 12-24 mesh screen (701-1397 microns) was used.
2. Synthetic seawater. Synthetic seawater is made by dissolving simulated sea salt mix, (Lake Product Co. Inc., St. Louis, Mo.) in distilled water. Simulated sea salt mix contains those elements found in natural sea salt in quantities greater than 0.004%.

3. Radioactive bromine. **Br was obtained by thermal neutron activation of ammonium bromide. A stock solution was made by dissolving the irradiated ammonium bromide in distilled water. An aliquot of the stock solution was added to synthetic sea water and stored in a polyethylene bottle.

APPARATUS

1. Exchange columns. Three columns were made, each consisting of a Pyrex tube (0.77 cm i.d.) with a glass frit on the bottom. A thin layer of glass wool was placed above the glass frit and the columns were each loaded with a water slurry of HgBr. Column 1 was filled to a height of 1.5 cm, column 2 to a height of 4.5 cm and column 3 to a height of 13.5 cm. The dry weight of HgBr used for each column was 1, 3 and 9 g, respectively.

2. Vacuum pump. A Duo Seal pump was used to draw the seawater through the column into a suction flask attached to the bottom of the column.

3. Vacuum gage. In order to obtain reproducible flow rates, a gage which measures the vacuum in inches of mercury was used. Vacuum was adjusted by bleeding air into the system through a stopcock (see Figure 1).

4. Gamma ray counter. A 3 in. x 3 in. sodium iodide [NaI(Tl)] scintillation detector with a well was used. It was encased in a 3 in. thick lead shield.

PROCEDURE

Seawater **Br activity was passed through the columns containing HgBr at various flow rates. The percentage of the radioactive bromide ions retained by the HgBr was calculated by the equation:

\[
\text{% retention} = \frac{\text{Br(B)} - \text{Br(A)}}{\text{Br(B)}} \times 100
\]

where:

\[
\text{Br(B)} = \text{**Br activity in seawater before passage through HgBr}
\]

\[
\text{Br(A)} = \text{**Br activity in seawater after passage through HgBr}
\]

A series of runs were made on each of three HgBr columns in accordance with the flow-rates and residence times shown in Table 1. The corresponding volume of seawater used in each run is also shown in Table 1. The apparatus used for these measurements is shown in Figure 1.
The rate of desorption of $^{86}\text{Br}$ from $\text{Hg}_2\text{Br}_3$ was also studied. For this study, a 13.5 cm and a 1.5 cm $\text{Hg}_2\text{Br}_3$ bed with adsorbed $^{86}\text{Br}$ were each washed with four 10 ml aliquots of seawater which did not contain $^{86}\text{Br}$. The four washings were passed through each column at a flow rate of 0.37 ml/cm$^2$-sec in rapid succession. The percentage of the radioactive-bromide ions desorped from the $\text{Hg}_2\text{Br}_3$ was calculated by the equation:

$$\%\text{ desorption} = \frac{\text{Br}(D)}{\text{Br}(O)} \times 100$$

where:

- $\text{Br}(D) = ^{86}\text{Br}$ activity desorbed from the $\text{Hg}_2\text{Br}_3$ bed with each seawater wash
- $\text{Br}(O) = ^{86}\text{Br}$ activity on the $\text{Hg}_2\text{Br}_3$ bed before the four seawater washings

**RESULTS**

A statistical analysis of the data was performed with the aid of a computer and are presented in Table 2. A description of the statistical treatment of the data obtained in a factorial experiment such as this may be found in standard texts on experimental statistics. For each of the three main factors: volume (A), flow rate (B) and amount of $\text{Hg}_2\text{Br}_3$ (C), a quasi F-ratio is computed in accordance with the approximation

$$F = \frac{MS(A) + MS(ABC)}{MS(AB) + MS(AC)}$$

that applies to a Model II (random effects) three-factor experimental design. Degrees of freedom for numerator and denominator are approximated by the Standard Satterthwaite formula. Replications of each experiment were not done and thus it was not possible to evaluate the random error; consequently, there is no check on the significance of a third-order interaction. The mean square for the third-order interaction is used in computing F-ratios for each of the second order interactions. Thus, the F-ratios for AB, AC and BC in Table 2 are the ratios of the "mean square" of the second order interaction to the "mean square" of the third order interaction (ABC). By comparing the F-ratios in Table 2 with the critical F value tabulated by Fisher and Yates\(^2\) for tests of significance, it is seen that in the ranges studied the amount of $\text{Hg}_2\text{Br}_3$, flow-rate, residence time as well as the interactions between these factors all have significant effects on the isotopic exchange of $^{86}\text{Br}$ with $\text{Hg}_2\text{Br}_3$.

The observations in Table 1 are also presented in plotted form in Figure 2. From Figure 2, it can be seen that the isotopic exchange of $^{86}\text{Br}$ with $\text{Hg}_2\text{Br}_3$ increases with column height, decreases with flow rate, and, to a lesser extent, decreases with residence time.

The data obtained in the desorption study are presented in Table 3. Initially, the radioactive bromide ions are rapidly desorbed, but the rate of desorption diminishes with time.
CONCLUSION

The results, when compared to those obtained for AgBr, as reported in reference (1), indicate that HgBr₂ can concentrate the bromide ions slightly better than AgBr and the seawater can desorb the bromide ions from HgBr₂ at a faster rate than from AgBr. The optimization of the concentration system would involve trade-offs between amounts of HgBr₂ used, flow-rates and counting system.
FIG. 1 APPARATUS USED FOR THE ISOTOPIC EXCHANGE
FIG. 2  RETENTION OF BROMIDE IONS BY ISOTOPIC EXCHANGE IN Hg₂Br₂ COLUMNS

FLOW RATE = 0.37 ml/cm²/sec
FLOW RATE = 0.89 ml/cm²/sec
FLOW RATE = 1.76 ml/cm²/sec
TABLE 1
ISOTOPIC RETENTION OF $^{82}$BR WITH MERCURIOUS BROMIDE

<table>
<thead>
<tr>
<th>Volume (ml)</th>
<th>Residence Time (sec)</th>
<th>Bromine Retention (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Col. 1 (1.5 cm)</td>
<td>Col. 2 (4.5 cm)</td>
</tr>
<tr>
<td>Flow-rate = 0.37 ml/cm²/sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>27.8</td>
<td>52.4</td>
</tr>
<tr>
<td>15</td>
<td>90</td>
<td>19.4</td>
<td>39.5</td>
</tr>
<tr>
<td>48</td>
<td>270</td>
<td>15.0</td>
<td>29.2</td>
</tr>
<tr>
<td>Flow-rate = 0.89 ml/cm²/sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>16.4</td>
<td>36.6</td>
</tr>
<tr>
<td>39</td>
<td>90</td>
<td>12.8</td>
<td>23.9</td>
</tr>
<tr>
<td>115</td>
<td>270</td>
<td>7.6</td>
<td>13.0</td>
</tr>
<tr>
<td>Flow-rate = 1.76 ml/cm²/sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>12.4</td>
<td>20.2</td>
</tr>
<tr>
<td>72</td>
<td>90</td>
<td>9.5</td>
<td>13.8</td>
</tr>
<tr>
<td>245</td>
<td>270</td>
<td>6.5</td>
<td>10.3</td>
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### TABLE 2

STATISTICAL ANALYSIS OF THE DATA

<table>
<thead>
<tr>
<th>Factors</th>
<th>Degrees of Freedom</th>
<th>Sum of Square of Deviations (SS)</th>
<th>Mean Squares (MS)</th>
<th>F ratio</th>
</tr>
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<tbody>
<tr>
<td><strong>Single Factors</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume (A)</td>
<td>2</td>
<td>1791</td>
<td>896</td>
<td>7.2</td>
</tr>
<tr>
<td>Flow rate (B)</td>
<td>2</td>
<td>2783</td>
<td>1391</td>
<td>10.0</td>
</tr>
<tr>
<td>Hg$_2$Br$_2$ (C)</td>
<td>2</td>
<td>5124</td>
<td>2562</td>
<td>11.7</td>
</tr>
<tr>
<td><strong>Interactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume x Flow rate (AB)</td>
<td>4</td>
<td>68</td>
<td>16.9</td>
<td>5</td>
</tr>
<tr>
<td>Volume x Hg$_2$Br$_2$ (AC)</td>
<td>4</td>
<td>388</td>
<td>96.9</td>
<td>32</td>
</tr>
<tr>
<td>Rate x Hg$_2$Br$_2$ (BC)</td>
<td>4</td>
<td>493</td>
<td>123</td>
<td>41</td>
</tr>
<tr>
<td>Volume x Flow rate x Hg$_2$Br$_2$ (ABC)</td>
<td>8</td>
<td>25.2</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 3

DESORPTION OF $^{82}\text{Br}$ FROM $\text{Hg}_2\text{Br}_2$

<table>
<thead>
<tr>
<th>Seawater Washes (10 ml aliquots)</th>
<th>$^{82}\text{Br}$ Desorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>24.7</td>
</tr>
<tr>
<td>Second</td>
<td>21.0</td>
</tr>
<tr>
<td>Third</td>
<td>9.0</td>
</tr>
<tr>
<td>Fourth</td>
<td>5.7</td>
</tr>
</tbody>
</table>

$^{82}\text{Br}$ remaining on $\text{Hg}_2\text{Br}_2$ bed after 4 washes

<table>
<thead>
<tr>
<th></th>
<th>9g</th>
<th>1g</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>40.2</td>
<td>25.6</td>
</tr>
</tbody>
</table>

TOTAL RECOVERY

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>99.6</td>
<td>100.7</td>
</tr>
</tbody>
</table>
REFERENCES