ELECTROCHEMICAL DETERMINATION OF TRIHALOMETHANES IN DRINKING WATER BY STRIPPING ANALYSIS

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Trihalomethanes (THMs), including CHCl$_3$, CHBrCl$_2$, CHBr$_2$Cl, and CHBr$_3$, are contaminants in drinking water that arise from disinfection by chlorine. Trihalomethanes, even at low levels, constitute one of the largest categories of environmental pollutants. These compounds are associated with significant health issues—toxicity, mutagenicity, carcinogenicity, and teratogenicity.$^{1-4}$ Consequently, the Environmental Protection Agency (EPA) has limited the total amount of THMs in drinking water to 80 µg/L.$^{5,6}$ With the aid of gas chromatography the EPA method can achieve detection limits of 1.6 and 0.02 µg L$^{-1}$ for bromoform and chloroform, respectively.$^7$ However, gas chromatography is lacking in portability and short analysis times, so electrochemical methods have been sought as alternative procedures. Accordingly, in this research, the method of stripping analysis$^8$ was chosen because the detection limit can be extended to the 10$^{-9}$ to 10$^{-10}$ M range.

To determine the concentration of trihalomethanes in a water sample, a three-step procedure is used. First, we employ controlled-potential electrolysis to reduce the THM at a silver cathode to form halide ions. Second, we collect (preconcentrate) this free halide by using the same silver electrode as an anode, held at a chosen potential for a prescribed time, to form a silver halide film. Third, we reduce (strip) the silver halide film by means of a prescribed time, to form a silver halide film. Third, we reduce (strip) the silver halide film by means of differential pulse voltammetry (DPV); the area of the resulting cathodic peak permits the determination of the concentration of trihalomethane (based on the method of standard addition).

Before stripping analysis could begin, we first had to optimize (a) the reduction potentials for trihalomethanes; (b) the electrolysis time needed to dehalogenate the THMs fully; (c) the potential at which a silver halide film would be deposited; (d) the deposition time; and (e) the scan rate for the stripping step.

Cyclic voltammetry was employed to determine the reduction potentials for the THMs. Figure 1 shows the forward scan of the cyclic voltammograms taken with each THM in water containing 0.010 M tetraethylammonium benzoate: (A) background; (B) 5.0 mM CHCl$_3$; (C) 5.0 mM CHBrCl$_2$; (D) 5.0 mM CHBr$_2$Cl; and (E) 5.0 mM CHBr$_3$.

Once the optimizations were established, stripping analysis with the method of standard addition was applied. In the table below, each calculated (found) value for bromoform is the average of at least 2 trials with a confidence limit of 95%. This method has also been applied to samples of each of the THMs alone as well as drinking water samples obtained from the city of Bloomington, IN.

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**Comparison of Known and Found Concentrations of Bromoform Determined by Means of Stripping Analysis with the Method of Standard Addition**

<table>
<thead>
<tr>
<th>Known (µg L$^{-1}$)</th>
<th>Found (µg L$^{-1}$)</th>
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<tbody>
<tr>
<td>182</td>
<td>170 ± 22</td>
</tr>
<tr>
<td>113</td>
<td>109 ± 4</td>
</tr>
<tr>
<td>76</td>
<td>66 ± 1</td>
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<tr>
<td>33</td>
<td>23 ± 7</td>
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</tbody>
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**References**