ABSTRACT

MEASUREMENT AND ANALYSIS OF BROMATE ION REDUCTION IN SYNTHETIC GASTRIC JUICE

by Jason Dimitrius Keith

Bromate ion is a possible carcinogen that is regulated by the US EPA at a Maximum Contamination Level (MCL) of 10 µg/L in drinking water. In order to propose an improved scientifically appropriate bromate ion MCL, a more rigorous scientific methodology is needed for determining low level dose health risks. The objectives of this research project were to measure bromate ion with oxidizing and/or reducing agents typically ingested in foods and drinking water.

The loss of bromate ion in HCl is too slow for significant reduction in the stomach. Addition of $10^{-5}$ M H$_2$S, a gastric juice component, decreases the half-life from 153 to 14 minutes. The ingested reducing agents iodide ion, nitrite ion, and iron(II) decrease the lifetime of bromate ion in the stomach. Chlorine, monochloramine, and iron(III) have little actual effect on the lifetime of bromate ion. The measured rates and chemical details of the reactions are discussed.
MEASUREMENT AND ANALYSIS OF BROMATE ION REDUCTION IN SYNTHETIC GASTRIC JUICE

A Thesis

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Department of Chemistry

by

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INTRODUCTION

Bromate Ion Chemistry and Human Toxicology

Ozonation has many advantages as a drinking water disinfectant. Ozone is a strong oxidant and can effectively control taste and odor causing compounds, remove color caused by humic compounds, and inactivate microorganisms such as Cryptosporidium oocysts (von Gunten 2002). However, disinfection of drinking water with ozone has some drawbacks such as the formation of inorganic and organic byproducts. The major drawback of ozonation is the formation of bromate ion in bromide ion containing waters (Gordon 1997). Bromide ion is present in surface waters due to geological formations, saltwater intrusion, and human activities (Siddiqui 1995). Bromide ion levels in US rivers and groundwaters typically average from 90 to 110 µg/L (Siddiqui 1995). These bromide ion levels can form significant amounts of bromate ion. The concentration and rate of bromate ion formation is also dependent on water and ozone characteristics such as pH, natural organic matter concentration, water temperature, ozone dose concentration, and ozone dose contact time.

The formation of bromate ion in bromide ion containing waters via ozonation is through a series of oxidation processes. The direct ozonation pathway developed by Haag and Hoigne is described by the following mechanism (Haag 1983):

\[ \text{Br}^- + \text{O}_3 \rightarrow \text{OBr}^- + \text{O}_2 \] \[ \text{OBr}^- + \text{H}^+ \rightarrow \text{HOBr} \] \[ \text{OBr}^- + \text{O}_3 \rightarrow \text{BrO}_2^- + \text{O}_2 \] \[ \text{OBr}^- + \text{O}_3 \rightarrow \text{Br}^- + 2 \text{O}_2 \] \[ \text{BrO}_2^- + \text{O}_3 \rightarrow \text{BrO}_3^- + \text{O}_2 \]

The mechanism shows that the initial reaction of ozone and bromide ion forms hypobromite ion and oxygen. The hypobromite ion can react with acid to form hypobromous acid, as shown in Equation [2]. The hypobromite ion can also react with ozone to form bromite ion or bromide ion, as shown in Equations [3] and [4]. The formation of bromate ion occurs
when hypobromite ion reacts with ozone to form bromite ion, which reacts with ozone to form bromate ion. The reactions also form oxygen, which is a decomposition product of ozone.

Disinfection of drinking water can also be accomplished with sodium hypochlorite. Sodium hypochlorite is formed from the reaction of sodium hydroxide and chlorine. The formation of sodium hypochlorite is (Orica Chloralkali 2005):

\[ \text{Cl}_2 \ (g) + 2 \text{NaOH} \ (aq) = \text{NaOCl} \ (aq) + \text{NaCl} \ (aq) + \text{H}_2\text{O} \ (l) \]  

[6]

Sodium hydroxide and chlorine are produced from the electrolysis of sodium chloride. Sodium chloride contains bromide ion, which is oxidized to bromate ion in the manufacturing process of the sodium hypochlorite solutions. Therefore, drinking water containing sodium hypochlorite can contain bromate ion. The stoichiometric reaction of bromide ion and hypochlorite ion to form bromate ion is (Weinberg 2003):

\[ \text{Br}^- + 3 \text{OCl}^- = \text{BrO}_3^- + 3 \text{Cl}^- \]  

[7]

According to the World Health Organization, one of the major problems with bromate ion in drinking water is that bromate ion is a possible human carcinogen. Bromate ion is also regulated by the US EPA at a Maximum Contamination Level (MCL) of 10 µg/L (Wagner 2000). The MCL was partly determined from animal studies that led to a projected potential lifetime risk of cancer from bromate ion exposure at \(10^{-4}\) at 5.0 µg/L and \(10^{-5}\) at 0.5 µg/L (Wagner 2000). The US EPA typically regulates carcinogens in drinking water in the range of \(10^{-4}\) to \(10^{-6}\) and concludes that an MCL in that range is safe and protective of public health. Even though a projected cancer risk of 10 µg/L for bromate ion would be associated with a lifetime risk greater than \(10^{-4}\), the MCL was selected as the Practical Quantitation Level (PQL) at that time. This PQL was selected because accurate and precise measurements at less than 10 µg/L were difficult to obtain by public water system laboratories due to a lack of affordable, sophisticated instrumentation, as well as expertise (Keith 2005). However, new analytical methods have a detection limit with more affordable instrumentation of 1.0 µg/L and it has been suggested that the MCL be lowered (Himat 1997).

There have also been suggestions of raising the MCL. The animal studies and models used to determine the health risks may have inherent flaws (Keith 2005; Weinberg 1998).
Determination of potential lifetime cancer risks to humans at different concentrations of bromate ion is made by administering high doses of bromate ion over a short period of time (the approximate laboratory animal’s lifetime), which are scaled to humans and their lifetime by observing incidences of cancer (Tanaka 1984). The doses administered to the laboratory animals are much higher than a human would ever experience from drinking water. It is the observed effects of the doses to the laboratory animals in conjunction with predictive models that are used to project the risks to humans at normal exposure levels.

There are two broad types of models that are used to estimate the effects of chemicals: linear (non-threshold) dose-response models and threshold models (Hogue 2004). Linear dose-response models extrapolate from the experimental data through zero after numerous modifications based upon the particular model being used, as shown in Figure 1a. They assume that a zero response occurs only when the dose is zero. The assumption made by these models is that there is a finite, albeit small, risk at any dose of a genotoxic carcinogen. Some form of this model is used for nearly all genotoxic carcinogens.

Threshold models are also used to estimate low dose effects. This model “assumes that there is an exposure concentration, or threshold, for the chemical that is considered to be safe” (Hogue 2004). In other words, there is a concentration of the chemical below which it is unlikely to cause an adverse effect under normal exposure levels, as shown in Figure 1b.

Each of these models can be used for estimating the effects of low level doses, but there are major problems associated with each model. These models rely on a number of default assumptions due to a lack of detailed data in some areas. One problem is that initial concentra-
tions used for the extrapolations are so high that high dose effects may overburden the animal’s detoxification system resulting in an overestimation of the low level effects. This in turn can result in the overestimation of the risk at low doses. Another common assumption is that the potential toxin remains unaffected by the environment after ingestion. In this example, no bromate ion would decompose or react with any other compounds prior to uptake. These inherent flaws within the models may potentially lead to an overestimation of the risk.

It is known that under acidic conditions, bromate ion in gastric juice will react with chloride ion and/or bromide ion (Schulek 1960). The stoichiometric reaction of bromate ion with chloride ion in acidic conditions is:

\[
\text{BrO}_3^- + 5 \text{Cl}^- + 6 \text{H}^+ = 2 \text{Cl}_2 + \text{BrCl} + 3 \text{H}_2\text{O} \quad [8]
\]

Some of the intermediates formed in the reaction of bromate ion and hydrochloric acid are bromous acid and hypochlorous acid. It should be noted that the reactions are reversible and highly pH-dependent.

Equation [8] is important for understanding the bromate ion chemistry in gastric juice because hydrogen ion and chloride ion are major components of gastric juice. Gastric juice has a chloride ion concentration of 0.170 M, which corresponds to approximately 6 g/L (Hollander 1934) and a pH range of approximately 0.8 to 3.0. Given the known bromate ion chemistry and the composition of gastric juice, bromate ion should be at least partially reduced in gastric juice under conditions in the typical human stomach. As a result, there should be less bromate ion reaching the target cell as compared to the ingested dose.

There are many additional reducing and oxidizing agents present in gastric juice or ingested in foods and drinking water that may affect the rate of bromate ion reduction. The species of interest in this study include hydrogen sulfide, sulfite ion, chlorine, monochloramine, nitrite ion, iodide ion, ferric ion, and ferrous ion. Each of these species could have different effects on the rate of bromate ion reduction. However, there are some similarities among the reducing and oxidizing agent groups for the reaction of bromate ion. For example, the stoichiometric reaction of bromate ion with excess nitrite ion in the presence of acid is (Radhakrishnamurti 1984):

\[
\text{BrO}_3^- + 3 \text{NO}_2^- = \text{Br}^- + 3 \text{NO}_3^- \quad [9]
\]
The suggested mechanism for bromate ion reduction in the presence of nitrite ion and acid is:

\[ \text{BrO}_3^- + \text{NO}_2^- \rightarrow \text{BrO}_2^- + \text{NO}_3^- \] \[ \text{[10]} \]

\[ \text{BrO}_2^- + \text{NO}_2^- \rightarrow \text{HOBr} + \text{NO}_3^- \] \[ \text{[11]} \]

\[ \text{HOBr} + \text{NO}_2^- \rightarrow \text{Br}^- + \text{NO}_3^- \] \[ \text{[12]} \]

The Radhakrishnamurti mechanism shows that bromate ion reacts with excess nitrite ion to eventually form bromide ion. It should be noted that Equations [11] and [12] are not balanced. These mechanistic steps, as well as others throughout the thesis, are not necessarily balanced because these steps are intended to emphasize the role of the specific intermediates involved in the mechanism as compared to the overall stoichiometric equations. Also, the stoichiometric reactions use the “=” sign to denote equilibrium processes. Mechanistic steps use the traditional “→” and/or “↔”.

The results of the bromate ion reaction in the presence of nitrite ion show that bromate ion reduction occurs by two electron steps. Bromate ion reduction can also occur by one electron processes. The possible set of reactions for the reduction of bromate ion in the presence of hydrogen sulfide and reformation of bromate ion in the presence of chlorine is:

\[ \text{BrO}_3^- + \text{H}_2\text{S} \rightarrow \text{BrO}_2 \] \[ \text{[13]} \]

\[ 2 \text{BrO}_2 \rightarrow \text{BrO}_3^- + \text{BrO}_2^- \] \[ \text{[14]} \]

\[ \text{BrO}_2^- + \text{Cl}_2 \rightarrow \text{BrO}_3^- + 2 \text{Cl}^- \] \[ \text{[15]} \]

The reactions show that hydrogen sulfide reduces bromate ion to bromine dioxide. It disproportionates to reform bromate ion and bromite ion. The bromite ion also reacts with chlorine to reform bromate ion.
Prior Analytical Methodology

The measurement of bromate ion in the presence of hydrochloric acid and reducing or oxidizing agents could be potentially made using ion chromatography (Himat 1997), high performance liquid chromatography (Creed 1996; Cunningham 2000), or an ion chromatograph coupled to an inductively coupled plasma mass spectrometer (Weinberg 1998; Snyder 2005).

High performance liquid chromatography (HPLC) methods are used to measure bromate ion in food products, such as breads at levels from 0.010 – 1 mg bromate ion/kg of bread (Creed 1996; Cunningham 2000).

The ion chromatograph inductively coupled plasma mass spectrometer (IC-ICP-MS) is used to measure bromate ion in drinking water at sub-µg/L levels (Weinberg 1998), as well as in complicated matrices such as blood (Snyder 2005). The detection limit for bromate ion using IC-ICP-MS can be as low as 20 – 50 pg/L in drinking water. One problem with the IC-ICP-MS is that the instrument is expensive and costly to maintain.

Ion chromatography is commonly used in research laboratories and at water treatment facilities. A common method of detecting bromate ion with IC is with a conductivity detector. Unfortunately, the conductivity detector has a high bromate ion detection limit of approximately 10 µg/L (Yamada 1998). The detection limit with a conductivity detector can be significantly higher than 10 µg/L in the presence of chloride ion. The minimization of chloride ion interference, especially chloride ion and bromate ion peak overlap, is possible using a silver cartridge (Novatek Corporation 2001), injection of a large sample volume (Valsecchi 1999), or using a post column reagent (PCR) and spectrophotometer (Salhi 1999).

A silver cartridge reduces chloride ion interference when silver ion reacts with chloride ion to form a silver chloride precipitate. Excess silver ion from the silver cartridge is exchanged for hydrogen ion by passing the solution through a hydrogen ion cartridge. The silver cartridge does remove chloride ion, but inconsistent concentrations of chloride ion appears to be removed because the silver ion concentration in the cartridge may be variable (Novatek Corporation 2001). Another problem is that small concentrations of bromate ion are also removed by the silver cartridge as the formation constant for silver bromate is 5.5 X 10^{-5} (Sillen 1964). These problems introduce error into the measurement, which reduces accuracy and precision.
Injection of a large sample volume can reduce chloride ion and bromate ion peak overlap. The large sample volume increases the amount of bromate ion, as well as the bromate ion peak area. This allows for accurate and precise measurement of bromate ion (Valsecchi 1999).

An ion chromatograph with a post column reagent solution containing ammonium molybdate and potassium iodide eliminates chloride-bromate ion peak overlap. Chloride-bromate ion peak overlap is eliminated because the PCR solution reacts with only bromate ion to form tri-iodide ion (I$_3^-$), which is measured with a UV-Vis spectrophotometer (Salhi 1999). The chloride ion does not react with the post column reagent and is not detected by the spectrophotometer. However, column overloading due to high chloride ion concentrations limits available binding sites on the analytical column for bromate ion and causes bromate ion peak broadening. Even though there are some potential problems, this system was best suited for measuring bromate ion in high chloride ion solutions. Thus, this system was chosen for the study.

**Objectives**

The objectives of this research project were to develop an ion chromatographic method to accurately and reproducibly measure bromate ion in hydrochloric acid containing various reducing and/or oxidizing agents that are typically ingested in foods and drinking water. The goal of the measurements would be to determine how quickly or slowly bromate ion is decomposed in the stomach. The purpose of the measurements would be to determine if the ingestion of foods and drinking water containing these oxidizing and/or reducing agents markedly affects the rate of bromate ion loss. The final objective would be to understand more about the chemical details of these bromate ion reactions.

**METHOD DEVELOPMENT AND ESTABLISHMENT OF PROTOCOLS**

**Solution Preparation**

All solutions and standards were prepared from reagent grade chemicals. Potassium bromate was purchased from J.T. Baker Chemical Company. Hydrogen sulfide was purchased from Sigma-Aldrich. The chlorine gas was purchased from Matheson Gas Products, Inc. All other chemicals were purchased from Fisher Chemical. Deionized and triply-distilled water (TDW) was used for the preparation of all solutions. The TDW was prepared using a Barnstead NanoPure system.
The chemicals required for IC operation were carbonate eluent, post column reagent, and sulfuric acid. A 9.00 X 10^{-3} M carbonate eluent was prepared by dissolving 1.910 g of sodium carbonate (Certified ACS) in 2.000 L of TDW. Sulfuric acid solutions of 5.00 X 10^{-1} and 1.50 X 10^{-1} N were prepared by adding 28.00 and 8.500 mL, respectively of concentrated sulfuric acid (Certified ACS) and diluting to 2.000 L. An ammonium molybdate (Certified ACS) stock solution was prepared by dissolving 0.247 grams in 100.0 mL of TDW. The post column reagent was prepared by dissolving 8.620 g of potassium iodide (Certified ACS) in approximately 100 mL of TDW, adding 43.0 µL of ammonium molybdate stock solution, and diluting to 200.0 mL with TDW. The carbonate eluent and PCR were degassed with nitrogen prior to IC operation. The post column reagent solution was prepared fresh daily. The ammonium molybdate solution was prepared every 21 days. The carbonate eluent and sulfuric acid solutions were prepared as needed.

Bromate ion standards were prepared by dilution from a bromate ion stock solution. The 1.00 g/L bromate ion stock solution was prepared by dissolving 0.131 g of potassium bromate (purity 99.88 %) in 100.0 mL of TDW. A second stock solution was prepared by diluting a 1.00 mL aliquot of the 1.00 g/L bromate ion stock solution in 100.0 mL of TDW to a final concentration of 1.00 X 10^{-2} g/L. The bromate ion stock solutions were stored at 4°C for a maximum of 21 days. Bromate ion standards were prepared from the 1.00 X 10^{-2} g/L bromate ion stock solution in the appropriate solution as outlined in Table 1.

The effects of chloride ion concentration on ion chromatograph operation and bromate ion peak shape were studied. A 10.00 g/L chloride ion stock solution was prepared by dissolving 1.648 g of NaCl (Certified ACS) in 100.0 mL of TDW. A second stock solution of 1.00 X 10^{-2} g/L was prepared by diluting 100.0 µL of 10.00 g/L stock solution in 100.0 mL of TDW. The chloride ion stock solutions were stored at 4°C for a maximum of 21 days. Chloride ion standards were prepared in TDW using the appropriate stock solution and Table 2.

The hydrochloric acid solutions of 0.170, 0.100, 5.00 X 10^{-2}, and 1.00 X 10^{-2} M were prepared by adding 10.45, 6.15, 3.07, and 6.10 X 10^{-1} mL, respectively, of 4.07 M HCl and diluting to 250.0 mL with TDW. For the experiments that required 0.170 M Cl⁻, 1.023, 1.753, and 2.338 g of NaCl (Certified ACS) was added to the 0.100, 5.00 X 10^{-2}, and 1.00 X 10^{-2} M HCl solution, respectively and diluted to 250.0 mL with TDW.
Table 1
Preparation of Bromate Ion Standards

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<td>10.00</td>
<td>7.50</td>
<td>100.0</td>
</tr>
<tr>
<td>1.00 X 10^3</td>
<td>10.00</td>
<td>10.00</td>
<td>100.0</td>
</tr>
</tbody>
</table>
The rate of bromate ion reduction was studied in the presence of hydrochloric acid with the addition of hydrogen sulfide (H$_2$S), chlorine, monochloramine, iron(II), iron(III), iodide ion, and nitrite ion.

Concentrations of approximately 10$^{-4}$, 10$^{-5}$, and 10$^{-6}$ M H$_2$S were prepared from a saturated (~ 0.1 M) H$_2$S stock solution. The H$_2$S stock solution was prepared by adding approximately 1.20 g of Na$_2$S (Certified ACS), 3.10 mL of 4.07 M HCl, and diluting to 25.0 mL with TDW. The preparation of the 10$^{-4}$, 10$^{-5}$, and 10$^{-6}$ M H$_2$S solutions is outlined in Table 3.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Stock Solution (M)</th>
<th>Stock Solution Added (mL)</th>
<th>Second Stock Solution Volume (mL)</th>
<th>Second Stock Solution (M)</th>
<th>Second Stock Solution Added (mL)</th>
<th>Final Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10$^{-4}$</td>
<td>0.10</td>
<td>5.00 $\times$ 10$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td>250.0</td>
</tr>
<tr>
<td>10$^{-5}$</td>
<td>0.10</td>
<td>2.00 $\times$ 10$^{-1}$</td>
<td>100.0</td>
<td>2.0 $\times$ 10$^{-4}$</td>
<td>50.0</td>
<td>250.0</td>
</tr>
<tr>
<td>10$^{-6}$</td>
<td>0.10</td>
<td>2.00 $\times$ 10$^{-1}$</td>
<td>100.0</td>
<td>2.0 $\times$ 10$^{-4}$</td>
<td>5.00</td>
<td>250.0</td>
</tr>
</tbody>
</table>

The effect of iodide ion on the rate of bromate ion reduction was measured. A 1.000 g/L iodide ion stock solution was prepared by dissolving 0.131 g of potassium iodide (Certified ACS) in 100.0 mL of TDW. Dilutions were prepared from the stock solution.

The effect of nitrite ion on the rate of bromate ion reduction was measured. A 1.000 g/L nitrite ion stock solution was prepared by dissolving 0.149 g of sodium nitrite (Certified ACS) in 100.0 mL of TDW. Dilutions were prepared from the stock solution.

The effect of iron(II) on the rate of bromate ion reduction was measured. A 1.000 g/L iron(II) stock solution was prepared by dissolving 0.356 g of ferrous chloride (FeCl$_2$ · 4 H$_2$O) (Certified ACS) in 100.0 mL of TDW. Dilutions were prepared from the stock solution.

The effect of iron(III) on the rate of bromate ion reduction was measured. A 1.000 g/L iron(III) stock solution was prepared by dissolving 0.290 g of ferric chloride (Certified ACS) in 100.0 mL of TDW. Dilutions were prepared from the stock solution.
The effect of sulfite ion on the rate of bromate ion reduction was measured. A stock sulfite ion solution of 1.0 \times 10^{-3} \text{ M} was prepared by dissolving 0.032 \text{ g} of Na_{2}SO_{3} in 250.0 \text{ mL} of TDW. Dilutions were prepared from the stock solution.

Solutions were prepared for measurement with a liquid chromatography quadrupole mass spectrometer (LC-MS/MS). The measurements were made by Shane Snyder of Southern Nevada Water Authority. Two separate solutions were prepared for measurement. Solution A was prepared by mixing 2.09 \text{ mL} of 4.07 \text{ M} HCl and 22.91 \text{ mL} of TDW. Solution B was prepared by mixing 500.0 \mu\text{L} of bromate ion stock solution (1.00 \times 10^{-2} \text{ g/L}) and 24.50 \text{ mL} of TDW. Solutions A and B were prepared in duplicate. Solutions A and B were mixed at the time of measurement.

Bromate ion concentrations were measured with an ICP-MS. Bromate ion standards of 6.25 \times 10^{2}, 1.25 \times 10^{3}, 2.50 \times 10^{3}, and 3.75 \times 10^{3} \mu\text{g/L} were prepared in 0.170 \text{ M} HCl. The standards were diluted ten-fold for ICP-MS measurement. Bromate ion standards of 6.25 \times 10^{3}, 1.25 \times 10^{4}, 2.50 \times 10^{4}, and 3.75 \times 10^{4} \mu\text{g/L} were prepared in 0.170 \text{ M} HCl. The standards were diluted one hundred-fold for ICP-MS measurement. Bromate ion reduction was measured with samples of 2.56 \times 10^{3} and 2.50 \times 10^{4} \mu\text{g/L} bromate ion in 0.170 \text{ M} HCl. The samples were diluted ten-fold and one hundred-fold, respectively for ICP-MS measurement.

**Preparation and Measurement of Stock HOCl/Cl2 and ClNH2 Solutions**

A 750 \text{ mL} HOCl/Cl_{2} solution was prepared by adjusting the pH of TDW with 50 \% NaOH to 11.4\pm0.1. The pH 11.4 solution was bubbled with high purity chlorine gas for seven minutes. The pH of the solution after bubbling was approximately 2.0. The solution was transferred to a Nalgene bottle and refrigerated at 4 \text{ \degree C} for a maximum of seven days.

A 165 \text{ mL} ClNH_{2} solution was prepared by weighing 0.803 \text{ g} of ammonium chloride (Certified ACS) (Greenberg 1985). Approximately 160 \text{ mL} of HOCl/Cl_{2} solution was added to the ammonium chloride and the pH was adjusted to 8.20\pm0.05 with carbonate free NaOH. The solution was stored in a Nalgene bottle and refrigerated at 4 \text{ \degree C} for a maximum of seven days.

The concentration of HOCl/Cl_{2} or ClNH_{2} solutions was determined by iodometric titration. In order to measure the concentration of HOCl/Cl_{2} or ClNH_{2}, a sodium thiosulfate solution was standardized. The sodium thiosulfate concentration was measured using an automatic titrater (Radiometer Copenhagen VIT90 Video Titrator, ABU93 Triburette, and SAM
90 Sample Station). The sodium thiosulfate was titrated with an iodine solution of 0.500 g KI, 500.0 µL concentrated H₂SO₄, and 5.00 mL of 7.946 × 10⁻³ M KIO₃. The following equations were used to calculate the thiosulfate (S₂O₃²⁻) concentration:

\[ \text{IO}_3^- + 6 \text{H}^+ + 5 \text{I}^- = 3 \text{I}_2 + 3 \text{H}_2\text{O} \]  \[ \text{[16]} \]

\[ 2 \text{S}_2\text{O}_3^{2-} + \text{I}_2 = 2 \text{I}^- + \text{S}_4\text{O}_6^{2-} \]  \[ \text{[17]} \]

The standardized sodium thiosulfate was used to titrate solutions of 0.500 g of KI, 30.00 mL of phosphate buffer, pH 7, and 4.000 mL HOCl/Cl₂ or 10.00 mL ClNH₂. The volume and molarity of S₂O₃²⁻, as well as Equations [18] – [20], were used to calculate the concentration of HOCl/Cl₂ or ClNH₂.

\[ 2 \text{S}_2\text{O}_3^{2-} + \text{I}_2 = 2 \text{I}^- + \text{S}_4\text{O}_6^{2-} \]  \[ \text{[18]} \]

\[ \text{HOCl} + 2 \text{I}^- + \text{H}^+ = \text{I}_2 + \text{H}_2\text{O} + \text{Cl}^- \]  \[ \text{[19]} \]

\[ \text{NH}_2\text{Cl} + 2 \text{I}^- + \text{H}^+ = \text{NH}_3 + \text{I}_2 + \text{Cl}^- \]  \[ \text{[20]} \]

The concentrations of the HOCl/Cl₂ or ClNH₂ stock solutions were typically 1.008 and 0.203 g/L, respectively. Dilutions were prepared from the stock solutions.

**Measurement of Iron(II) and Iron(III) in Solution**

The following solutions were required for the measurement of iron(II) and iron(III) in solution: hydroxylamine solution, 0.170 M hydrochloric acid solution, sodium acetate solution, ammonium acetate buffer solution, potassium permanganate solution, stock iron solution, and phenanthranoline solution (Greenberg 1985). The hydroxylamine solution was prepared by dissolving 10.000 g of hydroxylamine hydrochloride (Certified ACS) in 100.0 mL of TDW. A sodium acetate solution was prepared by dissolving 200.000 g of sodium acetate (Certified ACS) in 800.0 mL of TDW. The ammonium acetate buffer solution was prepared by dissolving 250.000 g of ammonium acetate in 150.0 mL of TDW and adding 700.0 mL of glacial acetic acid. A potassium permanganate solution was prepared by dissolving 1.600 g of potassium permanganate (Certified ACS) in 500.0 mL of TDW. The phenanthranoline solution was prepared by heating a solution of 0.100 g of 1,10-phenanthranoline (Certified ACS) and
100.0 mL of TDW to 80 °C for five minutes. A stock iron solution was prepared by adding 20.00 mL concentrated sulfuric acid (Certified ACS) to 50.00 mL of TDW, dissolving 1.404 g of ferrous ammonium sulfate (Certified ACS), and adding potassium permanganate solution until a faint pink color remained. Iron standards were prepared from the stock iron solution.

The concentration of total iron in solution was measured. Exactly 50.00 mL of each iron standard was mixed with 2.00 mL of concentrated hydrochloric acid and 1.00 mL of hydroxylamine hydrochloride solution. The solution was heated until approximately 20 mL remained. The solution that remained after heating, as well as 10.00 mL of ammonium acetate buffer, and 1.33 X 10⁻¹ mL of phenanthranoline solution was diluted to 50.00 mL with TDW. After 10 minutes, the absorbance of this solution was measured at 510 nm with a UV-Vis spectrophotometer (Hewlett-Packard 8453). A calibration curve of absorbance versus concentration was plotted using Microsoft Excel.

A 1.00 g/L stock iron(II) solution was prepared by dissolving 0.702 g of ferrous ammonium sulfate \([\text{Fe(NH}_4\text{)}_2\text{(SO}_4\text{)}_2 \cdot 6 \text{H}_2\text{O}]\) (Certified ACS) in 100.0 mL of TDW. A 1.00 g/L stock iron(III) solution was prepared by dissolving 0.723 g of ferric nitrate \([\text{Fe(NO}_3\text{)}_3 \cdot 9 \text{H}_2\text{O}]\) (Certified ACS) in 100.0 mL of TDW. Standards were prepared from the 1.00 g/L stock iron(II) and iron(III) solutions in the presence of 0.170 M HCl. The total iron concentration was measured using the same procedure that was used to measure the calibration standards. The concentration of total iron in these solutions was calculated using the absorbance of the solutions and the calibration curve line equation.

The concentration of ferrous iron in solution was measured. Standards were prepared from the 1.00 g/L stock iron(II) and iron(III) solutions in the presence of 0.170 M HCl. A 50.00 mL aliquot of the diluted iron(II) or iron(III) solution in the presence of 0.170 M HCl, as well as 20.00 mL of phenanthranoline solution, and 10.00 mL of ammonium acetate buffer solution were diluted to 100.0 mL with TDW. After 5 minutes, the absorbance of the solution was measured at 510 nm with a UV-Vis spectrophotometer. The absorbance of the solution and the calibration curve line equation were used to calculate the concentration of ferrous iron. The concentration of ferric iron in solution was calculated by subtracting the ferrous iron concentration from the total iron concentration.
An experiment, with a detection limit of 0.1 mg/L, was designed to measure the concentration of iron(III) in a 10.0 mg/L iron(II) solution in the presence of 0.170 M HCl. The results show that iron(III) was not detected in the 10.0 mg/L iron(II) solution.

**Instrumentation.**

A Dionex model # ICS-2500 ion chromatograph was designed specifically for the measurement of bromate ion. This system uses a post column reagent (PCR) and a UV-Visible spectrophotometer to measure bromate ion, as shown in Figure 2.

**Figure 2.** Schematic of an IC-PCR system

A sample is introduced into the 1.30 mL/minute carbonate eluent flow stream by an AS40 autosampler and 225.0 µL sample loop. Larger particles in the sample are removed on the AG9-HC guard column, and separation of the sample into various components occurs on the AS9-HC analytical column. The eluent and sample are acidified by an ASRS-ULTRA suppressor (Wagner 2002).

The PCR is delivered into the system pneumatically and is acidified by an ASRS-ULTRA suppressor. The acidified PCR and acidified sample converge at a mixing T and mix thoroughly in the reaction coil, which is heated to 80 °C. The mixed sample and PCR produce a yellow color (tri-iodide ion, I₃⁻). The tri-iodide ion is measured with a UV-Visible detector at a wavelength of 352 nanometers. The experimental parameters were determined using US EPA Method 326.0 Revision 1.0 (Wagner 2002). Data acquisition and analysis of the sample was
accomplished using The Dionex Chromeleon Chromatography Management System Version 6.5. Manipulation of the data was accomplished using Microsoft Excel.

Bromate ion was measured with two separate mass spectrometer systems. Bromate ion was measured with an MDS Inc. API 4000 triple-quad LC-MS/MS, which is a quadrupole mass spectrometer. Bromate ion was measured with a Varian ICP-MS using an SPS-3 Autosampler. The ICP-MS data were analyzed using Varian ICP-MS Expert Software Version 1.1.

Initial IC Experiments

The IC was purchased new, and it was designed specifically for the measurement of bromate ion. For these reasons, initial experiments were designed to determine the bromate ion: Method Detection Limit (MDL), Minimum Reporting Level (MRL), average percent recovery, accuracy, and precision. These initial values were calculated using US EPA Method 326.0 Revision 1.0 (Wagner 2002).

Seven replicate samples of TDW were fortified with 2.0 µg/L bromate ion and measured. The precision (percent relative standard deviation) of the seven samples was calculated with the equation:

\[
\text{% RSD} = \left[ \left\{ \frac{1}{n-1} \sum (x_i - \text{avg})^2 \right\} \right]^{1/2} \times \text{100}
\]

where \( x \) corresponds to the bromate ion concentration measured in each sample, \( n \) is the number of samples, and \( \text{avg} \) is the mean value of the samples. The percent relative standard deviation of the system is 6.8 %, which is well within the 20 % required by the US EPA. The accuracy of seven 2.0 µg/L bromate ion samples was calculated with the equation:

\[
\text{Accuracy} = \left[ \sum (i = 1 \ldots 7) x_{\text{avg}} - x_i / x_i \right] \times \text{100}
\]

where \( \sum \) is the summation of errors of each sample, \( x_{\text{avg}} \) is the mean value of the seven samples, and \( x_i \) is the actual bromate ion concentration in each sample. The accuracy of the system is 4.5 %, which is within the 15 % accuracy requirement of the US EPA. The average percent recovery was calculated for seven replicate 2.0 µg/L bromate ion samples in TDW. The percent recovery equation is:

\[
\text{Percent Recovery} = \left[ \frac{(A - B)}{C} \right] \times \text{100}
\]
where \( A \) is the measured bromate ion concentration in the fortified sample, \( B \) is the measured bromate ion concentration in the unfortified sample, and \( C \) is the fortified concentration. The average percent recovery of the system is 103.2 %, which is within the US EPA range of 75 – 125 %.

The Method Detection Limit (MDL) was calculated by measuring seven replicate samples of TDW that were fortified with 2.0 \( \mu \)g/L of bromate ion on three separate days. The MDL was calculated using the equation:

\[
\text{MDL} = St(n - 1, 1 - \alpha = 0.99) \tag{24}
\]

where \( t(n - 1, 1 - \alpha = 0.99) \) is the student’s \( t \) value for the 99% confidence level with \( n - 1 \) degrees of freedom, \( n \) is the number of replicate samples, and \( S \) is the standard deviation of the replicate samples. The MDL was calculated to be 0.32 \( \mu \)g/L. The Minimum Reporting Level (MRL) is calculated using the MDL. The MRL equation is:

\[
\text{MRL} = \text{MDL} \times 3 \tag{25}
\]

where MDL is the method detection limit. The MRL is approximately 1.0 \( \mu \)g/L.

Initial experiments were also designed to determine the correlation coefficient, slope, and \( y \)-intercept of bromate ion standards in TDW. Seven sets of bromate ion standards were prepared and measured with the ion chromatograph. A typical calibration curve of the bromate ion standards is shown in Figure 3.

![Figure 3. Bromate ion calibration curve in TDW](image-url)
The results from these initial experiments indicate that the ion chromatograph was operating within US EPA requirements (Wagner 2002).

Improvements in Measurement of Bromate Ion in High Chloride Ion and HCl Solutions

Typically, real gastric juice has a relatively constant chloride ion concentration of 0.170 M, which corresponds to approximately 6 g/L (Hollander 1934). The desired range of bromate ion measurement in synthetic or real gastric juices is from less than 1 µg/L to 200.0 µg/L, which correlates to at least a 1 X 10^5 fold excess of chloride ion. Due to the large excess of chloride ion, experiments were designed to determine the effect of chloride ion concentration on bromate ion peak shape. Bromate ion standards from 1.0 – 100.0 µg/L, that contained 1.00 X 10^{-2} – 1.00 X 10^{3} mg/L chloride ion, were prepared in TDW. Bromate ion solutions with greater than 1.00 X 10^{2} mg/L chloride ion produced bromate ion peak broadening, as shown in Figure 4.

![Figure 4](image.png)

**Figure 4.** Effects of chloride ion on the bromate ion IC peak

The chromatograms in Figure 4 show that a bromate ion sample with no chloride ion produces a symmetric bromate ion peak with a flat baseline. However, solutions with greater than 1.00 X 10^{2} mg/L chloride ion produce broad, asymmetric bromate ion peaks. The broad, asymmetric peak presents a problem in that an unbiased decision must be made of how to assign the bromate ion peak baseline. The bromate ion concentration can vary greatly depending on how the peak baseline is drawn. In response to this problem, five-fold dilutions were used to reduce the chloride ion interference, as shown in Figure 5.
Calibration standards from 5 – 100 µg/L bromate ion in 1.000 g/L chloride ion were measured with and without a five-fold dilution. The non-dilution calibration standards typically resulted in a linear equation of $y = 1.010x - 0.229$ and a correlation coefficient of 0.983. The five-fold dilution (prior to measurement) calibration standards resulted in a linear equation of $y = 1.002x - 0.047$ and a correlation coefficient of 0.999. The results show that even though a dilution introduces an additional experimental step that adds a systematic error, the method produces a narrow bromate ion peak with a baseline that can be assigned accurately and reproducibly with ease.

In response to these results, samples of 10, 25, and 50 µg/L bromate ion were measured with and without a five-fold dilution five times each (n = 5 experiments) in 1.000 g/L chloride ion to determine the mean value ± standard deviation in µg/L, percent relative standard deviation (RSD) and accuracy (%), as shown in Table 4.

The results in Table 4 show that five-fold dilution improves the accuracy, while the percent relative standard deviation remains constant for all three concentrations. The five-fold dilution decreases the bromate ion detection limit from approximately 3.0 to 1.0 µg/L in the 1.000 g/L chloride ion solution by improving the bromate ion peak shape. A five-fold dilution reduces chloride ion interference, which decreases peak width and reduces the number of ways of assigning the bromate ion peak baseline. Thus, five-fold dilution significantly improves the accuracy and the detection limit.
Table 4
Bromate Ion Accuracy and Precision in 1000 mg/L Chloride Ion
Using Non-Dilution and Five-Fold Dilution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Non-Dilution</th>
<th>Five-Fold Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 5 experiments for each concentration</td>
<td></td>
</tr>
<tr>
<td>10 µg/L</td>
<td>Mean Value ± Standard Deviation (µg/L)</td>
<td>8.59±0.44</td>
</tr>
<tr>
<td>10 µg/L</td>
<td>% RSD</td>
<td>5.12</td>
</tr>
<tr>
<td>10 µg/L</td>
<td>Accuracy</td>
<td>14.1 %</td>
</tr>
<tr>
<td>25 µg/L</td>
<td>Mean Value ± Standard Deviation (µg/L)</td>
<td>20.6±0.98</td>
</tr>
<tr>
<td>25 µg/L</td>
<td>% RSD</td>
<td>4.76</td>
</tr>
<tr>
<td>25 µg/L</td>
<td>Accuracy</td>
<td>17.6 %</td>
</tr>
<tr>
<td>50 µg/L</td>
<td>Mean Value ± Standard Deviation (µg/L)</td>
<td>45.7±2.55</td>
</tr>
<tr>
<td>50 µg/L</td>
<td>% RSD</td>
<td>5.58</td>
</tr>
<tr>
<td>50 µg/L</td>
<td>Accuracy</td>
<td>8.60 %</td>
</tr>
</tbody>
</table>

The high chloride ion concentrations in gastric juice are due to hydrochloric acid in the stomach. The determination of bromate ion in hydrochloric acid can be problematic due to chloride ion interference and other factors, as shown in Figure 6.

![Figure 6. Effect of hydrochloric acid on the bromate ion peak shape](image-url)
The chromatograms in Figure 6 show that the presence of hydrochloric acid affects retention time and peak shape. In response to this problem, dilution and other techniques were used to develop two complementary methods for measuring bromate ion in the presence of hydrochloric acid. The two methods require a new calibration curve for each solution or set of operating conditions, which will eliminate the error associated with shifting retention times and changing peak shape. Calibration standards for each new calibration curve in hydrochloric acid require immediate measurement due to simultaneous bromate ion reduction.

A comparison of calibration standards from 1.00 to 200.0 µg/L bromate ion in 0.170 M HCl for the non-dilution and five-fold dilution methods resulted in a correlation coefficient for the non-dilution method of 0.999 and a line equation of $y = 0.998x + 0.121$. The correlation coefficient for the five-fold dilution method was 0.999, and the line equation was $y = 1.004x - 0.062$.

The line equation and correlation coefficient for bromate ion in hydrochloric acid were similar for both the five-fold dilution and non-dilution methods because the calibration curve for each solution significantly reduces the number of ways of assigning the bromate ion peak baseline.

In response to these results, the two methods were used to measure bromate ion reduction in hydrochloric acid, as shown in Table 5.

### Table 5
**Initial Bromate Ion Reduction in HCl Using Non-Dilution and Five-Fold Dilution Methods**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Non-dilution (µg/L)</th>
<th>Five-Fold Dilution (µg/L)</th>
<th>% Difference Between Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>203</td>
<td>202</td>
<td>0.5</td>
</tr>
<tr>
<td>15</td>
<td>188</td>
<td>191</td>
<td>1.6</td>
</tr>
<tr>
<td>30</td>
<td>176</td>
<td>177</td>
<td>0.6</td>
</tr>
<tr>
<td>60</td>
<td>155</td>
<td>157</td>
<td>1.3</td>
</tr>
<tr>
<td>100</td>
<td>134</td>
<td>131</td>
<td>2.3</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
<td><strong>1.3</strong></td>
</tr>
</tbody>
</table>
A comparison of the non-dilution and five-fold dilution methods in HCl resulted in an average difference between the two methods of 1.3 percent. This signifies that the two data sets are statistically indistinguishable.

In conclusion, the techniques of non-dilution and five-fold dilution were used to measure bromate ion in the presence of chloride ion. Five-fold dilution reduces chloride ion interference and produces narrower bromate ion peaks. The narrower peak reduces the number of ways of assigning the bromate ion peak baseline, which reduces variation of the bromate ion concentration. For these reasons, five-fold dilution improves the accuracy of bromate ion measurement in 1.000 g/L chloride ion, while the percent relative standard deviation remains nearly constant. The bromate ion method detection limit is reduced from 3.0 to 1.0 µg/L with a five-fold dilution.

Dilution and the development of a new calibration curve for each solution or set of operating conditions resulted in two complementary methods for measuring bromate ion in the presence of hydrochloric acid. A comparison of the two methods in the presence of hydrochloric acid shows that the line equation and correlation coefficient are similar. The measurement of bromate ion reduction using both methods resulted in a difference between the two methods of 1.3 percent. Therefore, either method can be used to measure bromate ion loss in hydrochloric acid with the addition of potential oxidizing and/or reducing agents. Thus, the method that did not require dilution was used for additional experiments.

**Bromate Ion Reduction Experimental Set-up**

A specific procedure was developed for the measurement of bromate ion reduction. The procedure was used for all bromate ion reduction experiments. Prior to the bromate ion reduction experiment, the pH of the matrix and a 200 µg/L bromate ion standard in the matrix was measured to confirm that the pH was in the specified range. The bromate ion calibration standards were prepared in the same matrix as the bromate ion reduction experiment and measured with the ion chromatograph. Check standards were measured before and after the calibration standards to confirm that the IC was performing properly.

After the calibration and check standards were measured, the temperature of 25.0 mL of the solution was raised to 37.0 °C in a water bath. A temperature of 37.0 °C was chosen in order to mimic human body temperature. The change in temperature throughout the experiment was less than 1.0 °C. A 200.0 µg/L bromate ion sample was prepared by diluting 500.0 µL of
1 X 10^{-2} g/L bromate ion stock solution in 25.0 mL of the solution. An initial concentration of 200 µg/L bromate ion was chosen for all bromate ion reduction experiments, instead of a normal human consumption of less than 10 µg/L, in order to minimize experimental error. The solution and sample were mixed, the experiment start time was recorded, and an aliquot was measured immediately with the ion chromatograph. The mixed 25.0 mL solution and bromate ion sample were returned to the water bath. After time intervals of 30 minutes, aliquots were removed and measured until at least a 50 % reduction of bromate ion had occurred. Check standards were measured after each sample in order to confirm that the ion chromatograph was operating properly as well as to estimate the error for the previous sample. Microsoft Excel was used to analyze the calibration standard and bromate ion reduction data. The developed procedure resulted in accurate and reproducible results. The results of a typical bromate ion reduction experiment at 37 °C in 0.170 M HCl are shown in Table 6.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>BrO_3^- (ug/L)</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>172</td>
<td>12</td>
</tr>
<tr>
<td>60</td>
<td>151</td>
<td>23</td>
</tr>
<tr>
<td>90</td>
<td>130</td>
<td>34</td>
</tr>
<tr>
<td>120</td>
<td>110</td>
<td>44</td>
</tr>
<tr>
<td>180</td>
<td>87</td>
<td>56</td>
</tr>
<tr>
<td>240</td>
<td>67</td>
<td>66</td>
</tr>
</tbody>
</table>

**Table 6**

**Bromate Ion Reduction in 0.170 M HCl**

**Measurement of Hydrogen Sulfide in Real Gastric Juice**

In order to measure hydrogen sulfide in real human gastric juice, method development was required (Orion Research 1980; Shanthi 1996). A sulfide ion stock solution was prepared by dissolving approximately 10.0 grams of Na_2S in 25.0 mL of deaerated TDW. A sulfide ion antioxidant buffer (SAOB) was prepared by adding 110.0 mL of concentrated NaOH, 67.000 g of disodium EDTA, and 35.000 g of ascorbic acid and diluting to 1.000 L with deaerated TDW. A sulfide ion/SAOB stock solution was prepared by adding 5.00 mL of stock sulfide ion solution,
250.0 mL of SAOB, and diluting to 500.0 mL with deaerated TDW. An iodine solution was prepared by adding 1.000 g KI, 10.00 mL of 7.946 X 10^-3 M KIO₃, and 1.00 mL of concentrated H₂SO₄ and diluting to 100.0 mL with deaerated TDW.

In order to determine the sulfide ion concentration in the solution, a sodium thiosulfate solution was standardized. The sodium thiosulfate was standardized using the same procedure that was used for the measurement of HOCl/Cl₂ or ClNH₂. The sulfide ion/SAOB stock solution was standardized using the standardized sodium thiosulfate solution and the equation:

\[ S^{2-} + I_2 \rightarrow S \ (s) + 2 I^- \]  \[ 26 \]

The standardized sulfide ion/SAOB stock solution was used to prepare standards of 1.13 X 10⁻¹ to 1.13 X 10⁻⁷ M. The standard potential (mV) of the calibration standards was measured using an Orion Research Incorporated sulfide ion selective electrode. A calibration curve of standard potential versus log of sulfide ion concentration was constructed, as shown in Figure 7.

\[ y = -27.961x - 876.09 \]
\[ R^2 = 0.994 \]

**Figure 7.** Sulfide ion calibration curve

A 1.00 mL real gastric juice sample was mixed with 25.0 mL of SAOB and diluted to 50.0 mL with deaerated TDW. The standard potential of the solution was measured using the sulfide ion selective electrode. The standard potential of the solution and the calibration curve line equation were used to calculate the concentration of sulfide ion in real gastric juice. The
sulfide ion concentration is proportional to the hydrogen sulfide concentration. The hydrogen sulfide concentration in real human gastric juice is 7.7 \times 10^{-5} \text{ molar.}

The method of standard additions was also used to measure the hydrogen sulfide concentration in real gastric juice. Nine additions for a total of 590.0 \mu\text{L} of 1.13 \times 10^{-1} \text{ M standard were added to a 50.0 mL solution containing 1.00 mL of gastric juice, 25.0 mL of SAOB, and 24.0 mL of TDW.} The graph of standard potential versus log of the total standard added is shown in Figure 8.

The results from the standard addition experiment show that the concentration of H_2S in real human gastric juice is 9.2 \times 10^{-5} \text{ M.} An average of the two methods is approximately 8.5 \times 10^{-5} \text{ M H}_2\text{S.} The difference in the two methods is \pm 10\%. The difference in the hydrogen sulfide concentration using the two methods is most probably due to the volatility of hydrogen sulfide.

![Graph showing standard addition of 0.113 M sulfide ion standard to real gastric juice](image)

**Figure 8.** Standard addition of 0.113 M sulfide ion standard to real gastric juice

**RESULTS/DISCUSSION**

**Bromate Ion Reduction in H^+ and Cl^-**

The major component of real gastric juice is hydrochloric acid. For this reason, bromate ion reduction was measured initially in various hydrogen ion and chloride ion solutions. The stoichiometric equation for the reaction of bromate ion in the presence of hydrogen ion and chloride ion is:
\[
\text{BrO}_3^- + 5 \text{Cl}^- + 6 \text{H}^+ = 2 \text{Cl}_2 + \text{BrCl} + 3 \text{H}_2\text{O}
\]

In order to compare the rate of bromate ion reduction under various conditions, the bromate ion half-life \((t_{1/2})\) was calculated from the experimental data. Bromate ion reductions were made at hydrogen ion concentrations ranging from 0.01 to 0.170 M, which corresponds to a pH range of 2.0 to 0.8. The Cl\(^-\) concentration was constant at 0.170 M. These concentration ranges are common in normal human stomachs.

A graph of bromate ion concentration (µg/L) vs. time (minutes) for bromate ion reduction at 37 °C in the presence of 0.170 M HCl is shown in Figure 9. It should be noted that the graph is not linear, and the correlation coefficient is < 0.97.

\[
y = -0.534x + 185.270 \\
R^2 = 0.969
\]

**Figure 9.** Non-linear graph of bromate ion reduction data with 0.170 M HCl

A graph of \(\ln\) bromate ion (µg/L) vs. time (minutes) for bromate ion reduction in the presence of 0.170 M HCl is shown in Figure 10. The graph is linear with a correlation coefficient of 0.998, which indicates that the loss of bromate ion is a first-order process.

The bromate ion half-lives for 0.010 M to 0.170 M H\(^+\) and 0.170 M Cl\(^-\) are shown in Table 7. The results show that as the H\(^+\) concentration decreases from 0.170 M (pH 0.8) to 0.01 M (pH 2), the bromate ion half-life increases from 153 minutes to ~ 30.2 days. The reason the rate of bromate ion reduction increases as the hydrogen ion concentration increases is that additional hydrogen ions bind to the oxygen atoms of bromate ion. This results in the transfer of
the partial charge on bromine and weakening of the Br–O bonds, which more readily allows the reduction of bromate ion by chloride ion.

![Graph](image)

**Figure 10.** Linear graph of bromate ion reduction data with 0.170 M HCl

<table>
<thead>
<tr>
<th>Table 7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bromate Ion Half-life with 0.170 M Cl(^-) and Varying H(^+) Concentration</strong></td>
</tr>
<tr>
<td>(0.170 \text{ M H}^+) &amp; (0.135 \text{ M H}^+) &amp; (0.100 \text{ M H}^+) &amp; (0.075 \text{ M H}^+) &amp; (0.05 \text{ M H}^+) &amp; (0.01 \text{ M H}^+)</td>
</tr>
<tr>
<td>(t_{1/2}) &amp; 153 min &amp; 238 min &amp; 7.6 hours &amp; 14.8 hours &amp; 30.6 hours &amp; 30.2 days</td>
</tr>
</tbody>
</table>

The results from these experiments are shown graphically in **Figure 11**. The graph of \(\ln\) Experimental Rate versus \(\ln\) H\(^+\) indicates that the overall order with respect to hydrogen ion for bromate ion reduction is nominally 2.00 ± 0.05. The order of two signifies that doubling the hydrogen ion concentration will quadruple the rate of bromate ion reduction. Thus, changes in acidity in the stomach markedly affect the rate of bromate ion reduction.

The concentration of chloride ion in real gastric juice is relatively constant at 0.170 M. However, a few experiments were designed to determine the effect of chloride ion concentration on bromate ion reduction. The results of typical bromate ion reduction experiments in the presence of 0.135 M H\(^+\) and 0.135 M Cl\(^-\) and in the presence of 0.135 M H\(^+\) and 0.170 M Cl\(^-\) are shown in Figure 12.
Figure 11. Rate order of hydrogen ion

Figure 12. (top) Bromate ion reduction with 0.135 M $H^+$ and 0.135 M $Cl^-$. (bottom) Bromate ion reduction with 0.135 M $H^+$ and 0.170 M $Cl^-$. 
The results in Figure 12 are linear with a correlation coefficient of 0.998. A comparison shows that bromate ion reduction is more rapid in the presence of 0.135 M H⁺ and 0.170 M Cl⁻.

The results of the experiments in the presence of varying chloride ion and constant hydrogen ion have been used to calculate the half-life for each experiment, as shown in Table 8. This shows that in the presence of 0.05 M H⁺/0.170 M Cl⁻ the half-life is approximately 31 hours, while the half-life in the presence of 0.05 M H⁺/0.05 M Cl⁻ is nearly 10 days. These results indicate that increasing the chloride ion concentration significantly increases the rate of bromate ion reduction.

### Table 8

<table>
<thead>
<tr>
<th>Concentration</th>
<th>-half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.135 M H⁺/0.170 M Cl⁻</td>
<td>238 min</td>
</tr>
<tr>
<td>0.135 M H⁺/0.135 M Cl⁻</td>
<td>323 min</td>
</tr>
<tr>
<td>0.100 M H⁺/0.170 M Cl⁻</td>
<td>7.57 hours</td>
</tr>
<tr>
<td>0.100 M H⁺/0.100 M Cl⁻</td>
<td>19.7 hours</td>
</tr>
<tr>
<td>0.075 M H⁺/0.170 M Cl⁻</td>
<td>14.8 hours</td>
</tr>
<tr>
<td>0.075 M H⁺/0.075 M Cl⁻</td>
<td>45.6 hours</td>
</tr>
<tr>
<td>0.05 M H⁺/0.170 M Cl⁻</td>
<td>30.6 hours</td>
</tr>
<tr>
<td>0.05 M H⁺/0.05 M Cl⁻</td>
<td>229 hours</td>
</tr>
</tbody>
</table>

The results from the experiments show that the overall order with respect to chloride ion for bromate ion reduction is 1.50 ± 0.05. The non-integral order suggests that bromate ion reduction is occurring through parallel pathways.

It is important to note that the results from the hydrogen ion and chloride ion experiments suggest that the bromate ion reduction rate in the presence of only HCl is too slow for a significant amount of bromate ion to be reduced while it is retained in the stomach.

### Determination of the Rate Law

The results of these experiments were used in the development of a preliminary rate law. The generalized form of the rate law in the presence of bromate ion and hydrochloric acid is:

\[-d[\text{BrO}_3^-]/dt = k[\text{BrO}_3^-]^m [\text{H}^+]^n [\text{Cl}^-]^p\]  \[27\]

The results of the experiments reported here show that the overall orders for bromate ion, hydrogen ion, and chloride ion are 1.0, 2.0, and 1.5, respectively. The rate constant, \(k\), is calculated using the following equation:
\[ k = \frac{k_{\text{obs}}}{[H^+]^{2.0} [Cl^-]^{1.5}} \]

where \( k_{\text{obs}} \) is the calculated slope for a graph of \( \ln \) bromate ion concentration versus time for each experiment. Thus, the preliminary one-term experimental rate law is:

\[ -d[BrO_3^-]/dt = 2.2[BrO_3^-] [H^+]^{2.0} [Cl^-]^{1.5} \]

The concentrations of bromate ion, hydrogen ion, and chloride ion are expressed in moles/liter, and the bromate ion reduction rate is expressed in minutes. The units of the rate constant are \( \text{L}^{3.5}\text{mol}^{-3.5}\text{min}^{-1} \).

The one-term rate law in the presence of bromate ion and hydrochloric acid can be rewritten as two terms that represent parallel pathways:

\[ -d[BrO_3^-]/dt = k_1[BrO_3^-] [H^+]^2 [Cl^-] + k_2[BrO_3^-] [H^+]^2[Cl^-]^2 \]

The two-term rate law constants, \( k_1 \) and \( k_2 \), are determined by plotting experimental rate/\([\text{BrO}_3^-][\text{H}^+]^2[\text{Cl}^-]\) versus \([\text{Cl}^-]\). The equation of the line is \( y = 3.83x + 0.283 \) and the correlation coefficient is 0.917. The rate constants, \( k_1 \) and \( k_2 \), are 0.28 L\(^3\)mol\(^{-3}\)min\(^{-1}\) and 3.8 L\(^4\)mol\(^{-4}\)min\(^{-1}\), respectively. The preliminary two-term experimental rate law is:

\[ -d[BrO_3^-]/dt = 0.28[BrO_3^-] [H^+]^2 [Cl^-] + 3.8[BrO_3^-] [H^+]^2 [Cl^-]^2 \]

The experimental bromate ion reduction rates and the calculated bromate ion reduction rates using the two-term rate law can be compared, as shown in Table 9. One objective of the research project was to develop a rate law that agrees within 10\% of the experimental bromate ion reduction rates. The two-term rate law agrees within 6\% of the experimental rates. Additional experiments to improve and expand the experimental rate law were not be performed because it would also be necessary to include the effect of the reduction product, bromide ion, in the experimental rate law because bromide ion reacts significantly faster with bromate ion than chloride ion. It is also important to restate that the rate of bromate ion reduction is slow in the presence of only hydrochloric acid. The presence of other reducing agents in the stomach should increase the bromate ion reduction rate and readily be used as “proof of concept” compounds.
Table 9
Comparison of Experimental Bromate Ion Reduction Rates and Calculated Bromate Ion Reduction Rates Using the Two-Term Experimental Rate Law

<table>
<thead>
<tr>
<th>H⁺ Concentration</th>
<th>Cl⁻ Concentration</th>
<th>Experimental Rate</th>
<th>Calculated Rate</th>
<th>% Difference in Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.170</td>
<td>0.17</td>
<td>6.88 X 10⁻⁹</td>
<td>6.96 X 10⁻⁹</td>
<td>1.2</td>
</tr>
<tr>
<td>0.135</td>
<td>0.135</td>
<td>3.11 X 10⁻⁹</td>
<td>2.89 X 10⁻⁹</td>
<td>7.1</td>
</tr>
<tr>
<td>0.135</td>
<td>0.170</td>
<td>4.35 X 10⁻⁹</td>
<td>4.30 X 10⁻⁹</td>
<td>1.1</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
<td>9.54 X 10⁻¹⁰</td>
<td>1.03 X 10⁻⁹</td>
<td>8.0</td>
</tr>
<tr>
<td>0.100</td>
<td>0.170</td>
<td>2.41 X 10⁻⁹</td>
<td>2.53 X 10⁻⁹</td>
<td>5.0</td>
</tr>
<tr>
<td>0.075</td>
<td>0.075</td>
<td>3.77 X 10⁻¹⁰</td>
<td>3.60 X 10⁻¹⁰</td>
<td>4.5</td>
</tr>
<tr>
<td>0.075</td>
<td>0.170</td>
<td>1.16 X 10⁻⁹</td>
<td>1.30 X 10⁻⁹</td>
<td>12.1</td>
</tr>
<tr>
<td>0.500</td>
<td>0.170</td>
<td>5.83 X 10⁻¹⁰</td>
<td>6.04 X 10⁻¹⁰</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Average                           5.3
Std. Deviation                   3.7

Bromate Ion Reduction with Inorganic Sulfur-Containing Compounds

A literature search reveals that gastric juice contains the inorganic sulfur-containing compound, hydrogen sulfide (Encyclopedia.laborlawtalk.com 2005). The measured concentration of hydrogen sulfide in a sample of real human gastric juice is approximately 8.5 X 10⁻⁵ M. Although the hydrogen sulfide concentration was known for this particular sample, the concentration may vary throughout the human population. For this reason, experiments were designed to study the effect of varying hydrogen sulfide and hydrogen ion with constant 0.170 M Cl⁻. The results of the hydrogen sulfide experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 10.

The results show that the addition of 10⁻⁴ – 10⁻⁶ M H₂S at different hydrogen ion concentrations significantly increases the rate of bromate ion reduction as compared to the presence of only hydrochloric acid. The data show that the bromate ion half-life decreases from 153 minutes in the presence of 0.170 M HCl to 2 minutes in the presence of 0.170 M HCl and 10⁻⁴ M H₂S. Thus, the combination of 0.170 M HCl and 10⁻⁴ M H₂S can effectively reduce bromate ion by more than 95 % in less than 10 minutes.
Table 10
Bromate Ion Half-life with 0.170 M Cl\textsuperscript{-} and Varying H\textsuperscript{+} and H\textsubscript{2}S

<table>
<thead>
<tr>
<th>Molar ratio of 200 µg/L BrO\textsubscript{3}\textsuperscript{-} to H\textsubscript{2}S</th>
<th>0 M H\textsubscript{2}S</th>
<th>10\textsuperscript{-4} M H\textsubscript{2}S</th>
<th>10\textsuperscript{-5} M H\textsubscript{2}S</th>
<th>10\textsuperscript{-6} M H\textsubscript{2}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t\textsubscript{1/2}</td>
<td>0.170 M H\textsuperscript{+}</td>
<td>0.170 M Cl\textsuperscript{-}</td>
<td>153 min</td>
<td>2 min</td>
</tr>
<tr>
<td>t\textsubscript{1/2}</td>
<td>0.100 M H\textsuperscript{+}</td>
<td>0.170 M Cl\textsuperscript{-}</td>
<td>7.6 hours</td>
<td>15 min</td>
</tr>
<tr>
<td>t\textsubscript{1/2}</td>
<td>0.075 M H\textsuperscript{+}</td>
<td>0.170 M Cl\textsuperscript{-}</td>
<td>14.8 hours</td>
<td>8 min</td>
</tr>
<tr>
<td>t\textsubscript{1/2}</td>
<td>0.05 M H\textsuperscript{+}</td>
<td>0.170 M Cl\textsuperscript{-}</td>
<td>30.6 hours</td>
<td>10 min</td>
</tr>
</tbody>
</table>

The significant increase in the rate of bromate ion reduction occurs because hydrogen sulfide is a good reducing agent. Hydrogen sulfide quickly reduces bromate ion and its bromine-containing intermediates to minimize the regeneration of bromate ion. The stoichiometric reaction of hydrogen sulfide and bromate ion is:

\[ 4 \text{BrO}_3^- + 3 \text{S}^{2-} = 4 \text{Br}^- + 3 \text{SO}_4^{2-} \] \[32\]

The most probable initial step in the reaction is:

\[ \text{BrO}_3^- + \text{H}_2\text{S} \rightarrow \text{BrO}_2^- \] \[33\]

The proposed reaction suggests that hydrogen sulfide reacts to form the bromine-containing intermediate, BrO\textsubscript{2}. The BrO\textsubscript{2} reacts with hydrogen sulfide to form BrO\textsubscript{2}. The BrO\textsubscript{2} reacts with hydrogen sulfide to eventually form bromide ion.

The bromine-containing intermediates can be oxidized to regenerate bromate ion if there is a small or no excess of hydrogen sulfide as compared to bromate ion. A possible reaction for the regeneration of bromate ion is:

\[ 2 \text{BrO}_2^- \rightarrow \text{BrO}_2^- + \text{BrO}_3^- \] \[34\]
The reaction proposes that \( \text{BrO}_2 \) disproportionates to reform bromate ion. This results in a decrease of the bromate ion reduction rate.

In the presence of \( 10^{-4} \text{ M H}_2\text{S} \), there is a large excess of hydrogen sulfide as compared to bromate ion. The large excess of hydrogen sulfide results in the rapid reduction of bromate ion and its intermediates to minimize the reformation of bromate ion. However, in the presence of \( 10^{-5} \text{ M H}_2\text{S} \), there is one-tenth the available hydrogen sulfide as compared to \( 10^{-4} \text{ M H}_2\text{S} \). This results in a decrease of the bromate ion reduction rate as compared to \( 10^{-4} \text{ M H}_2\text{S} \). The bromate ion half-life in the presence of \( 0.170 \text{ M HCl} \) and \( 10^{-4} \text{ M H}_2\text{S} \) is 2 minutes, and the bromate ion half-life in the presence of \( 0.170 \text{ M HCl} \) and \( 10^{-5} \text{ M H}_2\text{S} \) is 14 minutes. The decrease of the bromate ion reduction rate as compared to \( 10^{-4} \text{ M H}_2\text{S} \) is most probably because \( \text{BrO}_2 \) and \( \text{BrO}_2^- \) regenerate some bromate ion, as shown in Equation [34].

In the presence of \( 10^{-6} \text{ M H}_2\text{S} \), there is now an excess of bromate ion as compared to hydrogen sulfide. The decrease of available hydrogen sulfide results in an increase of the bromate ion half-life as compared to \( 10^{-4} \) and \( 10^{-5} \text{ M H}_2\text{S} \). The increase of the bromate ion half-life is most probably due to an insufficient amount of hydrogen sulfide to quickly remove bromate ion, \( \text{BrO}_2 \) and \( \text{BrO}_2^- \). However, it is important to note that \( 10^{-6} \text{ M H}_2\text{S} \) still has a significant effect on the bromate ion reduction rate as compared to the presence of only hydrochloric acid.

The results were used to calculate the overall order with respect to hydrogen sulfide and hydrogen ion for bromate ion reduction. A graph of log half-life versus log hydrogen sulfide concentration results in a line equation of \( y = -0.548x - 1.21 \) and a correlation coefficient of 0.937, which indicates that the order with respect to hydrogen sulfide is \( 0.55 \pm 0.05 \). Thus, an increase of the hydrogen sulfide concentration will have a less than first order effect on bromate ion reduction.

A graph of log half-life versus log hydrogen ion concentration indicates that the order with respect to hydrogen ion is approximately \( 1.10 \pm 0.04 \), as shown in Figure 13. Thus, increasing concentrations of hydrogen ion will have a slightly greater than first order effect on bromate ion reduction.
In conclusion, the addition of $10^{-4}$ to $10^{-6}$ M H$_2$S to HCl greatly increases the rate of bromate ion reduction in synthetic gastric juice. The $8.5 \times 10^{-5}$ M H$_2$S found in real human gastric juice should also have a significant effect on the bromate ion reduction rate in the stomach.

The effect on the rate of bromate ion reduction in the presence of commonly ingested chemicals was also of interest because these chemicals might markedly increase or decrease the rate of bromate ion reduction. Sulfite ion is not normally found in real gastric juice, but it is found in many wines. The concentration of sulfite ion that is typically added to wines is 50 – 150 mg/L. Sulfite ion is added to protect against oxidation, as well as unwanted yeast and bacteria that may form after the wine has fermented (Cain Vineyard & Winery 2005). The rate of bromate ion reduction was measured in the presence of hydrochloric acid and sulfite ion as a possible “proof of concept” experiment that would demonstrate that other commonly ingested chemicals also change the bromate ion half-life in the stomach. Concentrations of $1 \times 10^{-5}$ M (0.8 mg/L), $4 \times 10^{-5}$ M (3.2 mg/L), and $1 \times 10^{-4}$ M (8.0 mg/L) sulfite ion were added to 0.170 M HCl. The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 11.

The results show that sulfite ion significantly increases the rate of bromate ion reduction as compared to the presence of hydrochloric acid. The sulfite ion results are comparable to the hydrogen sulfide results.
The significant increase in the rate of bromate ion reduction occurs because sulfite ion is a good reducing agent. Sulfite ion quickly reduces bromate ion and its intermediates to minimize the reformation of bromate ion. The initial reaction most probably is:

$$\text{BrO}_3^- + \text{SO}_3^{2-} \rightarrow \text{BrO}_2^- + \text{SO}_4^{2-}$$  \[35\]

The reaction proposes that sulfite ion and bromate ion react to form sulfate ion and bromite ion by means of a two-electron transfer process. The bromite ion will react with sulfite ion to eventually form bromide ion.

The results show that the bromate ion half-life in the presence of 0.170 M HCl and $1 \times 10^{-4}$ M sulfite ion (8.0 mg/L) is 2 minutes. In wine, there is approximately 6 – 20 times more sulfite ion as compared to the sulfite ion used in the experiments reported here. Thus, the half-life of bromate ion in wine would be less than 10 seconds.

In conclusion, the consumption of wines containing sulfite ion should result in a rapid rate of bromate ion reduction. Thus, the consumption of a glass of wine should result in a bromate ion half-life of a few seconds.

### Commonly Ingested Compounds and Their Effect on Bromate Ion Reduction

#### Free Available Chlorine

The previous experiments show that the addition of hydrogen sulfide to hydrochloric acid has a significant effect on bromate ion reduction. The experiments also show that the concentration of hydrogen sulfide affects the rate of bromate ion reduction. For these reasons, experiments were designed to study the rate of bromate ion reduction in the presence of reducing and oxidizing agents with and without the addition of varying concentrations of hydrogen sulfide.

<table>
<thead>
<tr>
<th></th>
<th>0.170 M HCl</th>
<th>0.170 M HCl and $1 \times 10^{-5}$ M SO$_3^{2-}$</th>
<th>0.170 M HCl and $4 \times 10^{-5}$ M SO$_3^{2-}$</th>
<th>0.170 M HCl and $1 \times 10^{-4}$ M SO$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{1/2}$ min</td>
<td>153</td>
<td>15</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 11  
Bromate Ion Half-life with 0.170 M HCl and Varying Sulfite Ion
Free available chlorine (Cl₂, HOCI, OCl⁻), a disinfectant and strong oxidizing agent, can be found in drinking water distribution systems at residual concentrations of approximately 0.1 – 2 mg/L. The effect of bromate ion reduction by hydrogen sulfide (H₂S) in the presence of free available chlorine was measured. High concentrations were used in order to better understand and explain the associated reaction chemistry. Concentrations of 2, 4, and 10 mg/L free available chlorine were added to a 200 µg/L bromate ion sample at 37 °C in synthetic gastric juice (0.170 M HCl with and without H₂S). The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 12.

**Table 12**

<table>
<thead>
<tr>
<th>Molar ratio of 200 µg/L BrO₃⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>0.0 mg/L Cl₂</td>
<td>153 min</td>
<td>2 min</td>
<td>14 min</td>
</tr>
<tr>
<td>t₁/₂</td>
<td>2.0 mg/L Cl₂</td>
<td>200 min</td>
<td>19 min</td>
<td>43 min</td>
</tr>
<tr>
<td>t₁/₂</td>
<td>4.0 mg/L Cl₂</td>
<td>211 min</td>
<td>5 min</td>
<td>21 min</td>
</tr>
<tr>
<td>t₁/₂</td>
<td>10.0 mg/L Cl₂</td>
<td>210 min</td>
<td>2 min</td>
<td>50 min</td>
</tr>
</tbody>
</table>
Some important points of the Cl₂ data include:

- In the presence of 0.170 M HCl and 2, 4, or 10 mg/L Cl₂, the bromate ion reduction rate decreases by 35 % as compared to the presence of only 0.170 M HCl (153 – 207 ± 6 minutes).

- In the presence of 0.170 M HCl and 10⁻⁵ M H₂S, increasing Cl₂ concentrations cause the rate of bromate ion reduction to decrease.
  - The bromate ion reduction rate in the presence of 10 mg/L Cl₂ decreases by 260 % as compared to the absence of free available chlorine (14 – 50 minutes).

- In the presence of 0.170 M HCl and 10⁻⁶ M H₂S, increasing Cl₂ concentrations cause a decrease of the bromate ion reduction rate.
  - The bromate ion reduction rate in the presence of 10 mg/L Cl₂ decreases by 965 % as compared to the absence of free available chlorine (32 – 341 minutes).

The results show that a strong oxidizing agent decreases the rate of bromate ion reduction (the half-life increases). In the pH range of 6 – 12, the reformation of bromate ion in the presence of an oxidizing agent is described by the following set of reactions (Bousher 1990):

\[
\begin{align*}
2 \text{HOBr} & \rightarrow \text{BrO}_2^- + \text{Br}^- \quad [36] \\
\text{HOBr} + \text{BrO}_2^- & \rightarrow \text{BrO}_3^- + \text{Br}^- \quad [37]
\end{align*}
\]

The overall stoichiometric reaction is:

\[
3 \text{HOBr} = \text{BrO}_3^- + 2 \text{Br}^- \quad [38]
\]

This reaction scheme shows that bromite ion and hypobromous acid react to reform bromate ion. In the presence of free available chlorine in the 6 – 12 pH range, a possible set of reactions that would result in the reformation of bromate ion is (Furman 1998):

\[
\begin{align*}
\text{HOBr} + \text{HOCl} & \rightarrow \text{HBrO}_2^- + \text{Cl}^- \quad [39] \\
\text{HBrO}_2^- + \text{HOCl} & \rightarrow \text{BrO}_3^- + \text{Cl}^- \quad [40]
\end{align*}
\]
The overall stoichiometric reaction is:

$$\text{HOBr} + 2 \text{HOCl} = \text{BrO}_3^- + 2 \text{Cl}^- \quad [41]$$

This set of reactions shows that hypobromous acid reacts with HOCl to eventually reform bromate ion. The reformation of bromate ion appears to slow the rate of bromate ion reduction. In other words, bromate ion is reduced, and the reduction intermediate is reoxidized to reform bromate ion.

The results of the experiments in the absence of H$_2$S (column labeled 0 M H$_2$S) show that free available chlorine appears to slow the rate of bromate ion reduction. The rate of bromate ion reduction is slowed because the initial reaction of bromate ion and H$^+$ and Cl$^-$ form bromine-containing intermediates, which react with Cl$_2$ to reform bromate ion.

Not very much bromate ion is reformed when 10$^{-4}$ M H$_2$S is added to the 0.170 M HCl and free available chlorine solution as shown by the observed 2 – 5 minute half-lives. There is such an excess of H$_2$S that any intermediates formed from the reaction of H$_2$S and bromate ion are quickly reduced, which minimizes the possibility of reforming bromate ion.

However, bromate ion is reformed when 10$^{-5}$ or 10$^{-6}$ M H$_2$S is added to the HCl and Cl$_2$ solution. The half-life increases in the presence of 10$^{-5}$ M H$_2$S from 14 minutes in the absence of Cl$_2$ to 50 minutes in the presence of 10 mg/L Cl$_2$. The reformation of bromate ion occurs because there is only a small excess of H$_2$S in the presence of 10$^{-5}$ M H$_2$S and no excess in the presence of 10$^{-6}$ M H$_2$S. The excess of Cl$_2$ as compared to H$_2$S results in Cl$_2$ reoxidizing BrO$_2$ and BrO$_2^-$ to reform bromate ion before H$_2$S completely reduces bromate ion. Therefore, the apparent rate of bromate ion reduction is slower. It should be noted that as the H$_2$S concentration decreases, the bromate ion half-life should approach the bromate ion half-life in the presence of only 0.170 M HCl and Cl$_2$. However, in the presence of 10$^{-6}$ M H$_2$S and Cl$_2$ the measured half-lives are greater than the measured half-lives in the presence of only 0.170 M HCl and Cl$_2$. This is most probably the result of side reactions and bromate ion intermediates that are also capable of reforming bromate ion.

The rate of bromate ion reduction with hydrogen sulfide in the presence of an oxidizing agent, such as Cl$_2$, may appear to decrease because of the following set of reactions:

$$\text{H}_2\text{S} + \text{Cl}_2 \rightarrow \text{S} (s) + 2 \text{HCl} \quad [42]$$
or \[ \text{BrO}_3^- + \text{H}_2\text{S} \rightarrow \text{BrO}_2 \]  

[43]

\[ 2 \text{BrO}_2 \rightarrow \text{BrO}_3^- + \text{BrO}_2^- \]  

[44]

\[ \text{BrO}_2^- + \text{Cl}_2 \rightarrow \text{BrO}_3^- + 2 \text{Cl}^- \]  

[45]

Equation [43] shows how hydrogen sulfide reduces bromate ion to form BrO$_2$ by means of a one-electron process. This intermediate disproportionates to form bromate ion and BrO$_2^-$. The BrO$_2^-$ reacts with an oxidizing agent, such as Cl$_2$, to reform bromate ion, as shown in Equation [45]. This results in an increase of the half-life (5 to 21 to 273 minutes or 2 to 50 to 341 minutes).

Equations [42] – [45] show that an oxidizing agent such as Cl$_2$, can regenerate bromate ion in the presence of H$_2$S because H$_2$S is also reacting to form oxidized species such as sulfur. The decrease of available H$_2$S to react with bromate ion decreases the actual rate of bromate ion reduction. These effects on the rate of bromate ion reduction are dependent on the following rates of hydrogen sulfide loss as shown in the differential equations:

Rate of H$_2$S loss: \[ k_{\text{H}_2\text{S}} [\text{H}_2\text{S}] [\text{Cl}_2] \]  

[46]

Rate of H$_2$S loss: \[ k_{\text{BrO}_3^-} [\text{BrO}_3^-] [\text{H}_2\text{S}] \]  

[47]

In conclusion, the results from these experiments show that free available chlorine, a strong oxidizing agent, has little or no effect on the apparent rate of bromate ion reduction in the presence of 10$^{-4}$ M H$_2$S. In the absence of H$_2$S, free available chlorine decreases the rate by approximately 45 – 60 minutes. In the presence of 10$^{-5}$ and 10$^{-6}$ M H$_2$S, free available chlorine decreases the rate by as much as 36 and 309 minutes, respectively. The effects on bromate ion reduction are dependent on the rates of competing chemical reactions. The effect of 2 mg/L free available chlorine, much higher than typical residual concentrations observed in drinking water, is not as significant as compared to concentrations of 4 and 10 mg/L free available chlorine. Thus, the ingestion of concentrations of free available chlorine typically found in drinking water should have little effect on bromate ion reduction in real gastric juice.


Monochloramine

The disinfectant and mild oxidizing agent, ClNH₂, can be found in drinking water distribution systems at residual concentrations of approximately 0.1 – 2 mg/L. Monochloramine is not as strong of an oxidizing agent as HOCl/Cl₂. The effect of bromate ion reduction in the presence of ClNH₂ was measured. High concentrations were used in order to better understand and explain the associated reaction chemistry. Concentrations of 4 and 10 mg/L ClNH₂ were added to a 200 µg/L bromate ion sample at 37 °C in synthetic gastric juice (0.170 M HCl with and without H₂S). The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 13.

<table>
<thead>
<tr>
<th>Molar ratio of 200 µg/L BrO₃⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>0.0 mg/L ClNH₂</td>
<td>153 min</td>
<td>2 min</td>
<td>14 min</td>
</tr>
<tr>
<td>Molar ratio of 4.0 mg/L ClNH₂ to H₂S</td>
<td>Excess H₂S</td>
<td>Excess ClNH₂</td>
<td>Excess ClNH₂</td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 4.0 mg/L ClNH₂ to BrO₃⁻</td>
<td>Excess ClNH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂</td>
<td>4.0 mg/L ClNH₂</td>
<td>276 min</td>
<td>9 min</td>
<td>9 min</td>
</tr>
<tr>
<td>Molar ratio of 10.0 mg/L ClNH₂ to H₂S</td>
<td>Excess ClNH₂</td>
<td>Excess ClNH₂</td>
<td>Excess ClNH₂</td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 10.0 mg/L ClNH₂ to BrO₃⁻</td>
<td>Excess ClNH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂</td>
<td>10.0 mg/L ClNH₂</td>
<td>278 min</td>
<td>7 min</td>
<td>10 min</td>
</tr>
</tbody>
</table>

Some important points of the ClNH₂ data include:

- In the presence of 10⁻⁴ and 10⁻⁵ M H₂S, H₂S is in excess as compared to bromate ion.
The addition of 4 or 10 mg/L ClNH₂ to 0.170 M HCl and 10⁻⁴ M H₂S results in a bromate ion reduction rate that decreases by approximately 300 % as compared to the absence of ClNH₂ (2 – 8 ± 1 minutes).

The addition of 4 or 10 mg/L ClNH₂ to 0.170 M HCl and 10⁻⁵ M H₂S results in a bromate ion reduction rate that increases by approximately 29 % as compared to the absence of ClNH₂ (14 – 10 ± 1 minutes).

The addition of 4 mg/L ClNH₂ to 0.170 M HCl and 10⁻⁶ M H₂S results in a bromate ion reduction rate that decreases by approximately 620 % as compared to the absence of ClNH₂ (32 – 231 minutes).

In the presence of 10⁻⁶ M H₂S, bromate ion is in excess as compared to hydrogen sulfide.

The addition of 4 mg/L ClNH₂ to 0.170 M HCl and 10⁻⁶ M H₂S results in a bromate ion reduction rate that decreases by approximately 620 % as compared to the absence of ClNH₂ (32 – 231 minutes).

The rate of bromate ion reduction with ClNH₂ and 10⁻⁶ M H₂S is faster than the rate of bromate ion reduction in the presence of only 0.170 M HCl and ClNH₂.

The results of the experiments in the absence of H₂S (column labeled 0 M H₂S) show that ClNH₂ slows the rate of bromate ion reduction. The ClNH₂ decreases the rate of bromate ion reduction more than the thermodynamically stronger oxidizing agent, Cl₂. A decrease in the rate of bromate ion reduction is most probably due to the initial reaction of bromate ion and H⁺ and Cl⁻ or Br⁻ to form bromine-containing intermediates, such as BrO₂⁻. Bromite ion is oxidized by ClNH₂ to reform bromate ion. A possible set of reactions in the presence of H⁺ and ClNH₂ that could cause the reformation of bromate ion is:

\[
\text{BrO}_3^- + H^+ + Cl^- \rightarrow \text{BrO}_2^- \quad [48]
\]

\[
\text{BrO}_2^- + \text{ClNH}_2 + H_2O \rightarrow \text{BrO}_3^- + \text{NH}_4^+ + Cl^- \quad [49]
\]

This set of reactions shows that bromite ion reacts with ClNH₂ to reform bromate ion. Thus, the actual loss of bromate ion is decreased.

Bromate ion most probably is being reformed in the presence of 10⁻⁴ M H₂S and ClNH₂. The effect is small because there is an excess of H₂S. However, the decrease in the rate is greater in the presence of ClNH₂ as compared to Cl₂. The decrease in the rate of bromate ion reduction in the presence of H₂S and ClNH₂ is small because H₂S can reduce many of the intermediates quickly. However, there is still enough intermediate present to reform some
bromate ion. Hydrogen sulfide in the presence of an oxidizing agent, such as ClNH₂, may appear to decrease the rate because of the following set of reactions:

\[
\text{BrO}_3^- + \text{H}_2\text{S} \rightarrow \text{BrO}_2 \quad [50]
\]

\[
2 \text{BrO}_2 \rightarrow \text{BrO}_3^- + \text{BrO}_2^- \quad [51]
\]

\[
\text{BrO}_2^- + \text{ClNH}_2 + \text{H}_2\text{O} \rightarrow \text{BrO}_3^- + \text{NH}_4^+ + \text{Cl}^- \quad [52]
\]

This set of reactions proposes that hydrogen sulfide can reduce bromate ion to form BrO₂. The BrO₂ reacts to reform bromate ion and BrO₂⁻. The BrO₂⁻ can react with an oxidizing agent, such as ClNH₂, to also reform bromate ion.

The results in the presence of 10⁻⁵ M H₂S and ClNH₂ show that there is a small increase in the rate of bromate ion reduction as compared to the presence of only 10⁻⁵ M H₂S. A comparison of ClNH₂ and Cl₂ in 10⁻⁵ M H₂S shows that bromate ion reduction is significantly slower in the presence of Cl₂. The reason is most probably because Cl₂ is a stronger oxidizing agent as compared to ClNH₂ and bromate ion is in excess as compared to H₂S. Therefore, the intermediates that are formed in Equations [50] and [51] can not be completely removed by H₂S, which instead results in the reformation of bromate ion. It should be noted that as the H₂S concentration decreases in the presence of ClNH₂, the bromate ion half-life should approach the bromate ion half-life in the presence of only 0.170 M HCl and ClNH₂. However, in the presence of 10⁻⁶ M H₂S and Cl₂, the measured half-lives are greater than the measured half-lives in the presence of only 0.170 M HCl and Cl₂.

In conclusion, the results from these experiments show that ClNH₂ decreases the rate of bromate ion reduction by as much as 7 minutes in the presence of 10⁻⁴ M H₂S. There is a greater decrease in the rate in the presence of ClNH₂ as compared to Cl₂. At 10⁻⁵ M H₂S, ClNH₂ increases the rate of bromate ion reduction by approximately 5 minutes, while Cl₂ decreases the rate by as much as 36 minutes. In the presence of 10⁻⁶ M H₂S and ClNH₂, the rate of bromate ion reduction decreases by as much as 200 minutes. However, Cl₂ decreases the rate more than ClNH₂. This most probably occurs because Cl₂ is a better oxidizing agent. The absence of H₂S and the presence of ClNH₂ results in a significant decrease in the rate. A comparison of ClNH₂ and Cl₂ in the absence of H₂S shows that ClNH₂ decreases the rate more than Cl₂.
The results of these experiments suggest that the ingestion of concentrations of monochloramine typically found in drinking water should have little effect on bromate ion reduction in the stomach.

**Iodide Ion**

The reducing agent, iodide ion, is consumed daily from seafood, milk, and table salt (World Health Organization 1996). The average uptake of I⁻ is approximately 200 µg per day. The effect of bromate ion reduction in the presence of iodide ion was measured by adding concentrations of 1, 2, 5, and 10 mg/L I⁻ to a 200 µg/L bromate ion sample at 37 °C in synthetic gastric juice (0.170 M HCl with and without H₂S). The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 14.

Some important points of the iodide ion data include:

- In the presence of 0.170 M HCl and the absence of H₂S, the addition of iodide ion results in a bromate ion reduction rate that is dependent on the iodide ion concentration.
- In the presence of 10⁻⁴, 10⁻⁵, 10⁻⁶ M H₂S, the addition of 1 or 2 mg/L I⁻ decreases the bromate ion reduction rate as compared to the absence of iodide ion.
- In the presence of 10⁻⁴, 10⁻⁵, 10⁻⁶ M H₂S, the addition of 5 or 10 mg/L I⁻ increases the bromate ion reduction rate as compared to the absence of iodide ion.

The results of the experiments in the absence of H₂S (column labeled 0 M H₂S) show that iodide ion increases the rate of bromate ion reduction. The increase in the rate of bromate ion reduction in the presence of a reducing agent, such as iodide ion, is in contrast to the results in the presence of an oxidizing agent, such as monochloramine or chlorine. Thus, a reducing agent increases the rate of reduction of bromate ion and an oxidizing agent decreases the rate of reduction of bromate ion.
Table 14
Bromate Ion Half-life with 0.170 M HCl and Varying Iodide Ion and H₂S

<table>
<thead>
<tr>
<th>Molar ratio of 200 µg/L BrO₃⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂ 0.0 mg/L I⁻</td>
<td>153 min</td>
<td>2 min</td>
<td>14 min</td>
<td>32 min</td>
</tr>
<tr>
<td>Molar ratio of 1.0 mg/L I⁻ to H₂S</td>
<td>Excess H₂S</td>
<td>Excess H₂S</td>
<td>Excess I⁻</td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 1.0 mg/L I⁻ to BrO₃⁻</td>
<td>Excess BrO₃⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂ 1.0 mg/L I⁻</td>
<td>111 min</td>
<td>5 min</td>
<td>23 min</td>
<td>45 min</td>
</tr>
<tr>
<td>Molar ratio of 2.0 mg/L I⁻ to H₂S</td>
<td>Excess H₂S</td>
<td>Excess I⁻</td>
<td>Excess I⁻</td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 2.0 mg/L I⁻ to BrO₃⁻</td>
<td>Excess I⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂ 2.0 mg/L I⁻</td>
<td>66 min</td>
<td>4 min</td>
<td>22 min</td>
<td>34 min</td>
</tr>
<tr>
<td>Molar ratio of 5.0 mg/L I⁻ to H₂S</td>
<td>Excess H₂S</td>
<td>Excess I⁻</td>
<td>Excess I⁻</td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 5.0 mg/L I⁻ to BrO₃⁻</td>
<td>Excess I⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂ 5.0 mg/L I⁻</td>
<td>28 min</td>
<td>1 – 1.5 min</td>
<td>13 min</td>
<td>20 min</td>
</tr>
<tr>
<td>Molar ratio of 10.0 mg/L I⁻ to H₂S</td>
<td>Excess H₂S</td>
<td>Excess I⁻</td>
<td>Excess I⁻</td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 10.0 mg/L I⁻ to BrO₃⁻</td>
<td>Excess I⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂ 10.0 mg/L I⁻</td>
<td>16 min</td>
<td>1 – 1.5 min</td>
<td>8 min</td>
<td>11 min</td>
</tr>
</tbody>
</table>
The rate of bromate ion reduction is dependent on $\Gamma$ concentration. A plot of $\log$ bromate ion half-life (in minutes) vs. $\log$ iodide ion concentration (mg/L) is shown in Figure 14.

Figure 14 shows that the plot of $\log$ of bromate ion half-life versus $\log$ of iodide ion concentration is linear, and the equation of the line is $y = -0.85x + 2.06$. This indicates that the order of the reaction with respect to iodide ion is 0.85. The order of less than one shows that iodide ion is competing with other reducing agents to remove bromate ion. The reduction of bromate ion in the presence of acid and iodide ion is represented by the balanced stoichiometric equation:

$$\text{BrO}_3^- + 9 \Gamma^- + 6 \text{H}^+ = 3 \text{I}_3^- + \text{Br}^- + 3 \text{H}_2\text{O} \quad [53]$$

The initial steps in the reaction are most probably:

$$\text{BrO}_3^- + \Gamma^- + \text{H}^+ \rightarrow \text{BrO}_2 \quad [54]$$

$$\text{BrO}_2 + \Gamma^- + \text{H}^+ \rightarrow \text{BrO}_2^- \quad [55]$$

The steps propose that bromate ion reacts with iodide ion and hydrogen ion to form $\text{BrO}_2$. The $\text{BrO}_2$ continues to react with iodide ion and hydrogen ion to form $\text{BrO}_2^-$. 
A comparison of the molar ratios of the reducing agents, iodide ion and hydrogen sulfide, shows that the rate of bromate ion reduction is faster in the presence of hydrogen sulfide. Thus, hydrogen sulfide is a better reducing agent for bromate ion.

The results of the experiments in the presence of $10^{-4}$ M H$_2$S show that the addition of 1 or 2 mg/L I$^-$ slightly decreases the rate of bromate ion reduction as compared to the absence of I$^-$. The effect is minimal most probably because the reaction is already fast in the presence of $10^{-4}$ M H$_2$S and HCl. Therefore, the addition of iodide ion has little overall effect on the rate.

The results of the experiments in the presence of $10^{-5}$ or $10^{-6}$ M H$_2$S show that I$^-$ affects the rate of bromate ion reduction. A plot of log bromate ion half-life (in minutes) vs. log iodide ion concentration (mg/L) in the presence of $10^{-6}$ M H$_2$S is shown in Figure 15.

Figure 15 shows that the plot of log of bromate ion half-life versus log of iodide ion concentration is linear, and the equation of the line is $y = -0.61x + 1.69$. This indicates that the order of the reaction with respect to iodide ion is 0.6. The order of less than one indicates that iodide ion is competing with hydrogen sulfide to reduce bromate ion. A comparison of the 0.6 order in the presence of $10^{-6}$ M H$_2$S and the 0.85 order in the absence of H$_2$S shows that iodide ion has even less effect on the rate of bromate ion reduction in the presence of $10^{-6}$ M H$_2$S. Under these conditions, hydrogen sulfide is a better reducing agent for bromate ion.

\[ y = -0.61x + 1.69 \]

\[ R^2 = 0.978 \]

**Figure 15.** Bromate ion reduction with iodide ion and $10^{-6}$ M H$_2$S

The bromate ion reduction rate in the presence of $10^{-5}$ or $10^{-6}$ M H$_2$S and iodide ion increases as the concentration of iodide ion increases most probably because there is excess
iodide ion as compared to hydrogen sulfide and bromate ion. The iodide ion and hydrogen sulfide both react with bromate ion and its intermediates quickly. This results in an overall increase in the rate of bromate ion reduction.

The results in the presence of 10^{-6} M H_2S and iodide ion show that iodide ion causes a small change in the bromate ion reduction rate as compared to the presence of only 10^{-6} M H_2S. This is in contrast to the results with the oxidizing agents, Cl_2 or ClNH_2. The rate significantly decreases in the presence of 10^{-6} M H_2S and Cl_2 or ClNH_2 as compared to the presence of 10^{-6} M H_2S. Therefore, a reducing agent such as iodide ion in the presence of 10^{-6} M H_2S has only a small effect on the rate of bromate ion reduction. On the other hand, an oxidizing agent in the presence of 10^{-6} M H_2S significantly decreases the rate of bromate ion reduction because of the reformation of bromate ion.

An important trend that should be noted is that the rate of bromate ion reduction decreases in the presence of 10^{-4}, 10^{-5}, and 10^{-6} M H_2S with the addition of 1 or 2 mg/L I\(^-\), as compared to the absence of I\(^-\). At 1 mg/L I\(^-\) there is no excess of I\(^-\), and at 2 mg/L I\(^-\), there is only a small excess of I\(^-\). Reactions between bromate ion and hydrogen sulfide form BrO_2 and BrO_2\(^-\). The BrO_2\(^-\) is further reduced by iodide ion, while the BrO_2 disproportionate to regenerate bromate ion, as shown in Equation [56].

\[
2 \text{BrO}_2 \rightarrow \text{BrO}_3^- + \text{BrO}_2^- \quad [56]
\]

The disproportionation reaction results in the formation of bromate ion (an apparent decrease in the rate of bromate ion reduction). The decrease in the rate of bromate ion reduction does not occur with the addition of 5 or 10 mg/L I\(^-\) because there is a large excess of iodide ion. The excess iodide ion can reduce bromate ion and its intermediates before bromate ion can be regenerated. This results in more bromate ion being reduced.

In conclusion, the results from these experiments show that iodide ion has a small effect on bromate ion reduction at 10^{-4} M H_2S. The effect is small because the rate of bromate ion reduction is already fast. The addition of iodide ion, in the presence of only HCl, increases the rate of bromate ion reduction by as much as 137 minutes because iodide ion reduces bromate ion and its intermediates quicker than does chloride ion. However, a comparison of hydrogen sulfide and iodide ion molar ratios shows that hydrogen sulfide is a better reducing agent. The addition of iodide ion to 10^{-5} and 10^{-6} M H_2S has mixed effects on the rate of bromate ion reduction. The
addition of 1 or 2 mg/L iodide ion decreases the rate by as much as 13 minutes as compared to the absence of iodide ion. This occurs most probably because bromate ion and hydrogen sulfide react to form BrO₂, which disproportionates to regenerate bromate ion. However, the bromate ion reduction rate is faster in the presence of 5 or 10 mg/L iodide ion and H₂S as compared to the absence of iodide ion. The rate is faster most probably because there is enough iodide ion present to reduce bromate ion and its intermediates before bromate ion can be regenerated.

The ingestion of foods containing typical concentrations of iodide ion may result in a small decrease in the rate of bromate ion reduction in the stomach. However, the rate of bromate ion reduction in the presence of iodide ion should still be rapid.

**Nitrite Ion**

Nitrite ion (NO₂⁻) is consumed daily in processed meats such as hot dogs and bacon (Epley 2005). The average uptake of nitrite ion is 20 – 40 mg per day. The effect of bromate ion reduction in the presence of nitrite ion, a reducing agent, was measured. Concentrations of 1, 2, 5, and 10 mg/L nitrite ion were added to a 200 µg/L bromate ion sample at 37 °C in synthetic gastric juice (0.170 M HCl with and without H₂S). The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 15.

Some important points of the nitrite ion data include:

- In the presence of 0.170 M HCl and the absence of H₂S, the addition of nitrite ion results in a bromate ion reduction rate that is dependent on the nitrite ion concentration.
- In the presence of 0.170 M HCl and 10⁻⁵ M H₂S, there is an excess of hydrogen sulfide and nitrite ion as compared to bromate ion.
  - The increase of nitrite ion concentration results in a bromate ion reduction rate that increases.
- In the presence of 0.170 M HCl and 10⁻⁶ M H₂S, there is an excess of bromate ion as compared to hydrogen sulfide.
  - The increase of nitrite ion concentration results in a bromate ion reduction rate that increases.
  - The rate of bromate ion reduction decreases as compared to the absence of hydrogen sulfide.
<table>
<thead>
<tr>
<th>Molar ratio of 200 µg/L BrO₃⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>0.0 mg/L NO₂⁻</td>
<td>153 min</td>
<td>2 min</td>
<td>14 min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar ratio of 1.0 mg/L NO₂⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>1.0 mg/L NO₂⁻</td>
<td>20 min</td>
<td>1 – 1.5 min</td>
<td>5 min</td>
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<table>
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<th>Molar ratio of 2.0 mg/L NO₂⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>2.0 mg/L NO₂⁻</td>
<td>10 min</td>
<td>1 – 1.5 min</td>
<td>5 min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar ratio of 5.0 mg/L NO₂⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>5.0 mg/L NO₂⁻</td>
<td>5 min</td>
<td>1 – 1.5 min</td>
<td>1 – 1.5 min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molar ratio of 10.0 mg/L NO₂⁻ to H₂S</th>
<th>0 M H₂S</th>
<th>10⁻⁴ M H₂S</th>
<th>10⁻⁵ M H₂S</th>
<th>10⁻⁶ M H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₁/₂</td>
<td>10.0 mg/L NO₂⁻</td>
<td>1 – 1.5 min</td>
<td>1 – 1.5 min</td>
<td>1 – 1.5 min</td>
</tr>
</tbody>
</table>
The results of the experiments in the absence of H$_2$S (column labeled 0 M H$_2$S) show that nitrite ion greatly increases the rate of bromate ion reduction. A plot of log bromate ion half-life (in minutes) vs. log nitrite ion concentration (mg/L) is shown in Figure 16.

\[
y = -1.07x + 1.33
\]

\[
R^2 = 0.969
\]

Figure 16. Bromate ion reduction with nitrite ion and 0 M H$_2$S

Figure 16 shows that the plot of log of bromate ion half-life versus log of nitrite ion concentration is linear, and the equation of the line is \( y = -1.07x + 1.33 \). This indicates that the effect of nitrite ion is nominally first order. This is in contrast to an order of less than one for iodide ion. The order of one indicates that the reaction of nitrite ion with bromate ion is the main reaction occurring and that bromate ion loss is roughly proportional to the nitrite ion concentration.

The increase in the rate of bromate ion reduction occurs because nitrite ion is a good reducing agent. Nitrite ion reacts with bromate ion and its intermediates to minimize the regeneration of bromate ion. The stoichiometric reaction of nitrite ion and bromate ion is:

\[
\text{BrO}_3^- + 3 \text{NO}_2^- = \text{Br}^- + 3 \text{NO}_3^- \quad [57]
\]

The mechanism for the reduction of bromate ion in the presence of nitrite ion is (Radhakrishnamurti 1984):

\[
\text{BrO}_3^- + \text{NO}_2^- \rightarrow \text{BrO}_2^- + \text{NO}_3^- \quad [58]
\]
\[ \text{BrO}_2^- + \text{NO}_2^- \rightarrow \text{HOBr} + \text{NO}_3^- \]  \[59\]

\[ \text{HOBr} + \text{NO}_2^- \rightarrow \text{Br}^- + \text{NO}_3^- \]  \[60\]

The mechanism shows that bromate ion reacts with nitrite ion to form \( \text{BrO}_2^- \). The \( \text{BrO}_2^- \) reacts with nitrite ion to form HOBr, which reacts with nitrite ion to form bromide ion. Each step in the bromate ion reduction mechanism occurs by means of a two-electron transfer process.

A comparison of nitrite ion and iodide ion molar ratios in the presence of 0.170 M HCl shows that the rate of bromate ion reduction is more rapid in the presence of nitrite ion. However, a comparison of nitrite ion and hydrogen sulfide molar ratios shows that the bromate ion reduction rate is more rapid in the presence of hydrogen sulfide. Thus, hydrogen sulfide is the best reducing agent of these three reducing agents.

The results of the experiments in the presence of \( 10^{-4} \) M H₂S show that the addition of nitrite ion has little or no apparent affect on the rate of bromate ion reduction because the rate is already very rapid in the presence of \( 10^{-4} \) M H₂S and HCl. The absence of an oxidizing agent or one-electron reduction process results in no regeneration of bromate ion in the presence of \( 10^{-4} \) M H₂S, HCl, and nitrite ion. Therefore, the rate of bromate ion reduction appears to remain constant for all nitrite ion concentrations.

The results of the experiments in the presence of \( 10^{-5} \) M H₂S show that the addition of nitrite ion increases the rate of bromate ion reduction. At \( 10^{-5} \) M H₂S there is an excess of hydrogen sulfide and nitrite ion as compared to bromate ion. The combined excess of both reducing agents react faster with bromate ion as compared to the reaction of bromate ion with the individual reducing agents. This increase in the bromate ion reduction rate can be noted as the half-life decreases from 20 minutes in the presence of \( 1 \text{ mg/L NO}_2^- \) and the absence of H₂S or 14 minutes in the presence of \( 10^{-5} \) M H₂S and the absence of NO₂⁻ to 5 minutes in the presence of both \( 10^{-5} \) M H₂S and \( 1 \text{ mg/L NO}_2^- \). This increase in the rate of bromate ion reduction is due to hydrogen sulfide and nitrite ion completely reducing bromate ion and its intermediates, as shown in Equations [58] – [60], before the intermediates can regenerate bromate ion.

In the presence of \( 10^{-6} \) M H₂S and nitrite ion, there are mixed effects on the rate of bromate ion reduction. A plot of log bromate ion half-life (in minutes) vs. log nitrite ion concentration (mg/L) in the presence of \( 10^{-6} \) M H₂S is shown in Figure 17.
Figure 17 shows that the plot of $\log$ of bromate ion half-life versus $\log$ of nitrite ion concentration is linear, and the equation of the line is $y = -1.23x + 1.52$. This indicates that the order of the reaction with respect to nitrite ion is approximately 1.2. Thus, increasing concentrations of nitrite ion will have a greater than first order effect on bromate ion reduction.

The effect of nitrite ion concentration on the rate of bromate ion reduction can be described by the following two term rate law:

$$\text{Rate} = k_1 [\text{BrO}_3^-][\text{NO}_2^-] + k_2 [\text{BrO}_3^-][\text{NO}_2^-]^2 \tag{61}$$

The presence of $10^{-6}$ M H$_2$S and nitrite ion increases the rate of bromate ion reduction as compared to the presence of only $10^{-6}$ M H$_2$S. The half-life for bromate ion reduction in the presence of 5 mg/L NO$_2^-$ and $10^{-6}$ M H$_2$S is 7 minutes, while the half-life in the presence of $10^{-6}$ M H$_2$S and absence of nitrite ion is 32 minutes.

The presence of $10^{-6}$ M H$_2$S and nitrite ion decreases the rate of bromate ion reduction as compared to the presence of only nitrite ion. The half-life for bromate ion reduction in 1 mg/L NO$_2^-$, and the absence of H$_2$S is 20 minutes, while the half-life in the presence of 1 mg/L NO$_2^-$ and $10^{-6}$ M H$_2$S is 30 minutes. This decrease in the rate in the presence of nitrite ion and $10^{-6}$ M H$_2$S most probably occurs because there is less available hydrogen sulfide to react with bromate ion and its intermediates and nitrite ion reacts with bromate ion and its intermediates at a slower rate as compared to hydrogen sulfide. Hydrogen sulfide reacts with bromate ion to form BrO$_2$, 

---

**Figure 17.** Bromate ion reduction with nitrite ion and $10^{-6}$ M H$_2$S
which disproportionates to form bromite and bromate ions, as shown in Equations [43] and [44]. The BrO$_2^-$ is further reduced by nitrite ion, as shown in Equation [59]. However, nitrite ion reduces bromate and bromite ions, as shown in Equations [58] – [60], at a slower rate as compared to hydrogen sulfide, which results in a decrease of the apparent loss of bromate ion.

A comparison of nitrite ion and iodide ion molar ratios in the presence of 10$^{-4}$, 10$^{-5}$, or 10$^{-6}$ M H$_2$S shows that the rate of bromate ion reduction is more rapid in the presence of nitrite ion. Thus, nitrite ion is a better reducing agent for bromate ion than iodide ion.

The oxidation potentials of nitrite ion, iodide ion, and hydrogen sulfide are $E^0 = -0.94$V, $E^0 = -0.54$V, and $E^0 = -0.14$V, respectively. In terms of thermodynamic driving forces, it might be expected that the initial step of bromate ion reduction would be most rapid in the presence of hydrogen sulfide and least rapid in the presence of nitrite ion. The experimental rates show that overall bromate ion reduction is least rapid in the presence of iodide ion and most rapid in the presence of hydrogen sulfide. Bromate ion reduction is most probably kinetically controlled, which means that the role of BrO$_2$ and BrO$_2^-$ markedly affect the rate at which each of the reducing agents remove and/or reform bromate ion.

In conclusion, the results from these experiments show that the addition of nitrite ion has little or no apparent effect on bromate ion reduction in the presence of 10$^{-4}$ M H$_2$S because the rate in the presence of only 10$^{-4}$ M H$_2$S is already rapid. There is an increase in the rate of bromate ion reduction by as much as 152 minutes in the absence of H$_2$S because nitrite ion reduces bromate ion and its intermediates quickly. In the presence of 10$^{-5}$ M H$_2$S, nitrite ion and hydrogen sulfide both remove bromate ion and its intermediates, which results in an increased rate of reduction as compared to the reaction of bromate ion with the individual reducing agents. In the presence of 10$^{-6}$ M H$_2$S and nitrite ion, the bromate ion reduction rate increases as compared to the absence of nitrite ion, but decreases as compared to the absence of H$_2$S. This effect is most probably a result of excess bromate ion as compared to hydrogen sulfide and a slower rate of reaction between nitrite ion and bromate ion.

The results of the experiments indicate that the consumption of foods containing as much as 10 mg/L nitrite ion may result in a small increase in the rate of bromate ion reduction in the stomach. Thus, the rate of bromate ion reduction should be quite rapid.
**Ferrous Ion**

Ferrous ion (Fe$^{2+}$) is commonly consumed in foods such as meats, poultry, and fish (PDR Health 2005). The average uptake of total iron (ferric and ferrous ion) is between 6 and 12 mg per day. The effect of bromate ion reduction in the presence of iron(II) was measured. Concentrations of 1, 2, 5, and 10 mg/L iron(II) were added to a 200 µg/L bromate ion sample at 37 °C in synthetic gastric juice (0.170 M HCl with and without H$_2$S). The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 16.

Some important points of the ferrous ion data include:

- The iron(II) solution contained less than 1 % of iron(III).
- The addition of iron(II) to 0.170 M HCl and the absence of H$_2$S results in a bromate ion reduction rate that is dependent on the iron(II) concentration.
- The addition of iron(II) to 0.170 M HCl and 10$^{-4}$ or 10$^{-5}$ M H$_2$S results in a constant effect on the bromate ion reduction rate as compared to the absence of iron(II).
  - In the presence of 1 – 10 mg/L iron(II), 0.170 M HCl, and 10$^{-4}$ M H$_2$S, the bromate ion reduction rate is 1 – 1.5 minutes.
  - In the presence of 1 – 10 mg/L iron(II), 0.170 M HCl, and 10$^{-5}$ M H$_2$S, the bromate ion reduction rate is 9 ± 1 minutes.

The results of the experiments in the absence of H$_2$S (column labeled 0 M H$_2$S) show that iron(II), a reducing agent, increases the rate of bromate ion reduction. A plot of log bromate ion half-life (in minutes) versus log iron(II) concentration (mg/L) is shown in Figure 18.

![Figure 18. Bromate ion reduction with iron(II) and 0 M H$_2$S](image)

\[ y = -0.58x + 1.97 \]

\[ R^2 = 0.992 \]
Table 16
Bromate Ion Half-life with 0.170 M HCl and Varying Fe$^{2+}$ and H$_2$S

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>0 M H$_2$S</th>
<th>10$^{-4}$ M H$_2$S</th>
<th>10$^{-5}$ M H$_2$S</th>
<th>10$^{-6}$ M H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio of 200 µg/L BrO$_3^-$ to H$_2$S</td>
<td>Excess H$_2$S</td>
<td>Excess H$_2$S</td>
<td>Excess BrO$_3^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>0.0 mg/L Fe$^{2+}$</td>
<td>153 min</td>
<td>2 min</td>
<td>14 min</td>
<td>32 min</td>
</tr>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Molar ratio of 1.0 mg/L Fe$^{2+}$ to H$_2$S</td>
<td>Excess H$_2$S</td>
<td>Excess Fe$^{2+}$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 1.0 mg/L Fe$^{2+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>1.0 mg/L Fe$^{2+}$</td>
<td>91 min</td>
<td>1 – 1.5 min</td>
<td>10 min</td>
<td>24 min</td>
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</tr>
<tr>
<td>Molar ratio of 2.0 mg/L Fe$^{2+}$ to H$_2$S</td>
<td>Excess H$_2$S</td>
<td>Excess Fe$^{2+}$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 2.0 mg/L Fe$^{2+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>2.0 mg/L Fe$^{2+}$</td>
<td>62 min</td>
<td>1 – 1.5 min</td>
<td>9 min</td>
<td>30 min</td>
</tr>
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</tr>
<tr>
<td>Molar ratio of 5.0 mg/L Fe$^{2+}$ to H$_2$S</td>
<td>Excess H$_2$S</td>
<td>Excess Fe$^{2+}$</td>
<td>Excess Fe$^{2+}$</td>
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<tr>
<td>Molar ratio of 5.0 mg/L Fe$^{2+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>5.0 mg/L Fe$^{2+}$</td>
<td>39 min</td>
<td>1 – 1.5 min</td>
<td>9 min</td>
<td>21 min</td>
</tr>
<tr>
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</tr>
<tr>
<td>Molar ratio of 10.0 mg/L Fe$^{2+}$ to H$_2$S</td>
<td>Excess Fe$^{2+}$</td>
<td>Excess Fe$^{2+}$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar ratio of 10.0 mg/L Fe$^{2+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>10.0 mg/L Fe$^{2+}$</td>
<td>23 min</td>
<td>1 – 1.5 min</td>
<td>8 min</td>
<td>14 min</td>
</tr>
</tbody>
</table>
shows that the plot of log of bromate ion half-life versus log of iron(II) concentration is linear, and the equation of the line is \( y = -0.58x + 1.97 \), which corresponds to the order of the reaction with respect to iron(II) of 0.6. This indicates that iron(II) is competing with other reducing agents to remove bromate ion. The stoichiometric reaction of iron(II) and bromate ion in the presence of acid is:

\[
\text{BrO}_3^- + 6 \text{Fe}^{2+} + 6 \text{H}^+ = 6 \text{Fe}^{3+} + \text{Br}^- + 3 \text{H}_2\text{O} \quad [62]
\]

The initial steps in the reaction of bromate ion with iron(II) in the presence of acid most probably are:

\[
\text{BrO}_3^- + \text{Fe}^{2+} + 2 \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{BrO}_2 + \text{H}_2\text{O} \quad [63]
\]

\[
\text{BrO}_2 + \text{Fe}^{2+} \rightarrow \text{BrO}_2^- + \text{Fe}^{3+} \quad [64]
\]

These mechanistic steps suggest that excess iron(II) and acid react with bromate ion to form \( \text{BrO}_2 \) and iron(III). The \( \text{BrO}_2 \) reacts with excess iron(II) in the presence of acid to form \( \text{BrO}_2^- \). The \( \text{BrO}_2^- \) will react with excess iron(II) and acid to eventually form bromide ion.

The increase of the rate of bromate ion reduction occurs because iron(II) is a good reducing agent. Iron(II) reacts with bromate ion, \( \text{BrO}_2 \), and \( \text{BrO}_2^- \) and minimizes the regeneration of bromate ion.

A comparison of iron(II), nitrite ion, and iodide ion molar ratios in the presence of 0.170 M HCl shows that the bromate ion reduction rate is the least rapid in the presence of iron(II) and the most rapid in the presence of nitrite ion. Thus, nitrite ion is the best reducing agent for bromate ion.

In the presence of \( 10^{-4} \) and \( 10^{-5} \) M H\(_2\)S, the bromate ion reduction rate is constant even in the presence of increasing iron(II) concentrations. The bromate ion half-life in the presence of \( 10^{-4} \) M H\(_2\)S and iron(II) is 1 – 1.5 minutes, and the half-life in the presence of \( 10^{-5} \) M H\(_2\)S and iron(II) is 9±1 minutes. The rate of reduction with changing iron(II) concentration is nearly constant because of a series of competing reactions. The reaction of iron(II) and bromate ion or \( \text{BrO}_2 \) forms iron(III), as shown in Equations [63] and [64]. The iron(III) that is formed can react with and remove hydrogen sulfide:
H$_2$S + 2 Fe$^{3+}$ $\rightarrow$ 2 Fe$^{2+}$ + 2 H$^+$ + S(s)  

The reaction of iron(III) and hydrogen sulfide results in the removal of hydrogen sulfide and formation of iron(II) and sulfur. The iron(II) that is formed can reduce additional bromate ion and BrO$_2$. This cycle results in a steady-state bromate ion reduction rate with iron(II) that is constant in the presence of 10$^{-4}$ and 10$^{-5}$ M H$_2$S.

The increase in the bromate ion reduction rate in the presence of 10$^{-4}$ M H$_2$S or 10$^{-5}$ M H$_2$S and iron(II) is minimal as compared to the presence of only 10$^{-4}$ M H$_2$S or 10$^{-5}$ M H$_2$S. The bromate ion half-life in the presence of 10$^{-4}$ M H$_2$S and iron(II) is 1 – 1.5 minutes, and the half-life in the presence of 10$^{-4}$ M H$_2$S is 2 minutes. The bromate ion half-life in the presence of 10$^{-5}$ M H$_2$S and iron(II) is 9±1 minutes, and the half-life in the presence of 10$^{-5}$ M H$_2$S is 14 minutes. The effect is minimal most probably because some hydrogen sulfide is removed by the reaction of iron(III) and hydrogen sulfide, as shown in Equation [65]. However, there is still sufficient hydrogen sulfide available to quickly reduce bromate ion, BrO$_2$, and BrO$_2^-$, which results in a rapid bromate ion reduction rate.

A comparison of nitrite ion and iron(II) in the presence of hydrogen sulfide shows that bromate ion reduction is more rapid in the presence of nitrite ion. In the presence of nitrite ion and hydrogen sulfide, both reducing agents quickly remove bromate ion, BrO$_2$, and BrO$_2^-$, which minimizes the reformation of bromate ion. In the presence of iron(II) and hydrogen sulfide, hydrogen sulfide is removed, as shown in Equation [65], which slows the overall bromate ion reduction rate.

The results of iodide ion and iron(II) reduction of bromate ion in the presence of hydrogen sulfide show that the concentration of the reducing agents affects the bromate ion reduction rate. In the presence of low concentrations (1 or 2 mg/L) of either iron(II) or iodide ion, the bromate ion reduction rate is faster in the presence of iron(II). In the presence of low concentrations of iron(II), less hydrogen sulfide is removed, as shown in Equation [65], which results in more available hydrogen sulfide to rapidly reduce bromate ion. In the presence of low concentrations of iodide ion, there is little or no excess of iodide ion as compared to bromate ion, which results in a slower bromate ion reduction rate. High concentrations (5 or 10 mg/L) of either iron(II) or iodide ion result in a bromate ion reduction rate that is similar for both reducing
agents. The rates are similar, most probably, because iron(II) removes more hydrogen sulfide, as shown in Equation [65], and there is more available iodide ion to react with bromate ion.

The experimental rates show that in the presence of hydrogen sulfide, the overall bromate ion reduction is least rapid in the presence of iodide ion and most rapid in the presence of nitrite ion. The oxidation potentials of nitrite ion, iron(II), and iodide ion are \(E^o = -0.94V\), \(E^o = -0.77V\), and \(E^o = -0.54V\), respectively. These potentials suggest that the thermodynamic driving forces for the initial step of bromate ion reduction should be the most rapid in the presence of iodide ion and the least rapid in the presence of nitrite ion. Bromate ion reduction is most probably kinetically controlled, which indicates that competing reactions with \(\text{BrO}_2\) and \(\text{BrO}_2^-\) affect the rate that reducing agents remove and/or regenerate bromate ion.

In conclusion, the results from these experiments show that bromate ion reduction in the presence of 0.170 M HCl and iron(II) increases by as much as 130 minutes as compared to the presence of only 0.170 M HCl because iron(II) quickly reduces bromate ion, \(\text{BrO}_2\), and \(\text{BrO}_2^-\) to minimize the reformation of bromate ion. In the presence of \(10^{-4}\), \(10^{-5}\), and \(10^{-6}\) M H\(_2\)S, both hydrogen sulfide and iron(II) quickly reduce bromate ion, which increases the bromate ion reduction rate. The bromate ion reduction rate in the presence of \(10^{-4}\) and \(10^{-5}\) M H\(_2\)S is nearly constant at 1 – 1.5 and 9 minutes, respectively, even with increasing iron(II) concentrations. The rate is constant most probably because iron(II) reacts with bromate ion to form iron(III), and the iron(III) reacts with hydrogen sulfide to reform iron(II). This cycle results in constant bromate ion half-lives.

The results of the experiments suggest that the consumption of foods containing as much as 10 mg/L iron(II) should have little effect on the rate of bromate ion reduction in the stomach.

**Ferric Ion**

Ferric ion (Fe\(^{3+}\)) is commonly consumed in foods such as dairy products and vegetables. The average uptake of total iron (ferric and ferrous ion) is between 6 and 12 mg per day. The effect of bromate ion reduction in the presence of iron(III) was measured. Concentrations of 1, 2, 5, and 10 mg/L iron(III) were added to a 200 µg/L bromate ion sample at 37 °C in synthetic gastric juice (0.170 M HCl with and without H\(_2\)S). The results of the experiments have been used to calculate the half-life for each bromate ion experiment, as shown in Table 17.
<table>
<thead>
<tr>
<th>Molar ratio of 200 µg/L BrO$_3^-$ to H$_2$S</th>
<th>0 M H$_2$S</th>
<th>10$^{-4}$ M H$_2$S</th>
<th>10$^{-5}$ M H$_2$S</th>
<th>10$^{-6}$ M H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>t$_{1/2}$ 10.0 mg/L Fe$^{3+}$</td>
<td>153 min</td>
<td>2 min</td>
<td>14 min</td>
<td>32 min</td>
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<table>
<thead>
<tr>
<th>Molar ratio of 1.0 mg/L Fe$^{3+}$ to H$_2$S</th>
<th>Excess H$_2$S</th>
<th>Excess Fe$^{3+}$</th>
<th>Excess Fe$^{3+}$</th>
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<tbody>
<tr>
<td>Molar ratio of 1.0 mg/L Fe$^{3+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{3+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$ 10.0 mg/L Fe$^{3+}$</td>
<td>182 min</td>
<td>4 min</td>
<td>35 min</td>
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<th>Excess H$_2$S</th>
<th>Excess Fe$^{3+}$</th>
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<tr>
<td>Molar ratio of 2.0 mg/L Fe$^{3+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{3+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$ 2.0 mg/L Fe$^{3+}$</td>
<td>181 min</td>
<td>5 min</td>
<td>39 min</td>
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<th>Molar ratio of 5.0 mg/L Fe$^{3+}$ to H$_2$S</th>
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<th>Excess Fe$^{3+}$</th>
<th>Excess Fe$^{3+}$</th>
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<tbody>
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<td>Excess Fe$^{3+}$</td>
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<td></td>
</tr>
<tr>
<td>t$_{1/2}$ 5.0 mg/L Fe$^{3+}$</td>
<td>154 min</td>
<td>5 min</td>
<td>42 min</td>
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<tr>
<th>Molar ratio of 10.0 mg/L Fe$^{3+}$ to H$_2$S</th>
<th>Excess Fe$^{3+}$</th>
<th>Excess Fe$^{3+}$</th>
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<tbody>
<tr>
<td>Molar ratio of 10.0 mg/L Fe$^{3+}$ to BrO$_3^-$</td>
<td>Excess Fe$^{3+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$ 10.0 mg/L Fe$^{3+}$</td>
<td>164 min</td>
<td>6 min</td>
<td>42 min</td>
</tr>
</tbody>
</table>
Some important points of the ferric ion data include:

- In the presence of iron(III), 0.170 M HCl, and 10^{-4}, 10^{-5}, or 10^{-6} M H_2S, the rate of bromate ion reduction decreases as compared to the absence of iron(III).
- The addition of iron(III) to 0.170 M HCl and 10^{-4}, 10^{-5}, or 10^{-6} M H_2S results in a constant effect on the bromate ion reduction rate as compared to the absence of iron(III).
  - In the presence of 1 – 10 mg/L iron(III), 0.170 M HCl, and 10^{-4} M H_2S, the bromate ion reduction rate is 5 ± 1 minutes.
  - In the presence of 1 – 10 mg/L iron(III), 0.170 M HCl, and 10^{-5} M H_2S, the bromate ion reduction rate is 40 ± 3 minutes.
  - In the presence of 1 – 10 mg/L iron(III), 0.170 M HCl, and 10^{-6} M H_2S, the bromate ion reduction rate is 87 ± 3 minutes.

The results show that in the presence of iron(III) and 10^{-4}, 10^{-5}, or 10^{-6} M H_2S, the rate of bromate ion reduction decreases as compared to the presence of only H_2S. The possible sets of reactions that may decrease the rate of bromate ion reduction are:

\[
\text{BrO}_3^- + \text{H}_2\text{S} \rightarrow \text{BrO}_2 \quad [43]
\]

\[
\text{BrO}_2 + \text{Fe}^{3+} \rightarrow \text{BrO}_3^- + \text{Fe}^{2+} \quad [66]
\]

or

\[
\text{H}_2\text{S} + 2 \text{Fe}^{3+} \rightarrow 2 \text{Fe}^{2+} + 2 \text{H}^+ + \text{S (s)} \quad [65]
\]

Equations [43] and [66] suggest that bromate ion is reduced by hydrogen sulfide to form BrO_2 and the BrO_2 reacts with iron(III) to reform bromate ion. Equation [65] indicates that iron(III) reacts with hydrogen sulfide. These reactions would result in less available hydrogen sulfide to react with bromate ion.

The decrease in the bromate ion reduction rate is affected by these competing reactions. The effect on the bromate ion reduction rate for each set of reactions is dependent on the rate of reaction for hydrogen sulfide with bromate ion and the rate of reaction for hydrogen sulfide with iron(III). If, the reaction of hydrogen sulfide with bromate ion is more rapid, then the bromate ion reduction rate is controlled by Equations [43] and [66]. However, if the reaction of hydrogen
sulfide with iron(III) is more rapid, then the bromate ion reduction rate is controlled by Equation [65].

On the other hand it should be noted that the source and oxidation state of iron(II) and iron(III) in the stomach is most probably not Fe(OH)_{6}^{2+} and/or Fe(OH)_{6}^{3+}. The iron species will most probably be complex species, such as FeCl_{2}^{+}, and/or other more complicated Fe^{3+} – ligand complexes. In the stomach, iron(III) may also form complexes with organic materials. Thus, the chemistry of the iron(III) species involved in the reduction of bromate ion becomes very complicated. It should be noted that the oxidation potential for each iron(III) complex will most probably vary significantly. As an example, the oxidation potential of Fe(CN)_{5}(NH_{3})^{3-} is E^o = -0.374V, the oxidation potential of Fe(CN)_{5}(H_{2}O)^{3-} is E^o = -0.491V, and the oxidation potential of Fe(CN)_{5}(NO_{2})^{3-} is E^o = -0.516V. The varying oxidation potentials of the iron(III) complexes suggests that their effect on bromate ion reduction is most probably quite different as compared to Fe(OH)_{6}^{3+}.

The results of the experiments in the presence of iron(III) and 10^{-4}, 10^{-5}, or 10^{-6} M H_{2}S indicate that the bromate ion reduction rate is relatively constant even in the presence of increasing iron(III) concentrations. The results in the presence of 10^{-4} M H_{2}S and iron(III) are 5 ± 1 minutes. The bromate ion half-life in the presence of 10^{-5} M H_{2}S and iron(III) is 40 ± 3 minutes, and the bromate ion half-life in the presence of 10^{-6} M H_{2}S and iron(III) is 87 ± 3 minutes. The results are constant most probably because iron(III) reacts with hydrogen sulfide to form iron(II), and the iron(II) reacts with bromate ion to form iron(III), as shown in Equations [63] and [65]. This cycle results in a steady-state bromate ion reduction rate with iron(III) that is constant in the presence of 10^{-4}, 10^{-5}, and 10^{-6} M H_{2}S.

A comparison of the oxidizing agents iron(III), Cl_{2}, and ClNH_{2} in the presence of hydrogen sulfide shows that there are mixed effects on the bromate ion reduction rate. The results in the presence of 10^{-4} M H_{2}S and iron(III) show that the bromate ion reduction rate is more rapid as compared to ClNH_{2} but less rapid as compared to Cl_{2}. The reduction rate in the presence of 10^{-5} M H_{2}S and iron(III) is significantly slower as compared to Cl_{2} and ClNH_{2}. In the presence of 10^{-6} M H_{2}S and iron(III), the reduction rate is significantly faster as compared to Cl_{2} and ClNH_{2}. The mixed effects on the bromate ion reduction rate in the presence of hydrogen sulfide and Cl_{2}, or ClNH_{2}, or iron(III) are most probably because the concentration of hydrogen sulfide affects each oxidizing agent differently. The concentration of hydrogen sulfide has
different effects on each oxidizing agent, which results in different rates of reduction and reformation of bromate ion. Thus, the bromate ion reduction rate varies for each oxidizing agent.

In conclusion, the results from these experiments show that the addition of iron(III) to 0.170 M HCl decreases the rate of bromate ion reduction by as much as 29 minutes. The bromate ion reduction rate also decreases in the presence of iron(III) and $10^{-4}$, $10^{-5}$, or $10^{-6}$ M H$_2$S. The decrease of the bromate ion reduction rate is most probably caused by the set of reactions shown in Equations [43] and [66] and/or Equation [65]. In the presence of iron(III) and $10^{-4}$, $10^{-5}$, or $10^{-6}$ M H$_2$S, the bromate ion reduction rate is constant at 5, 40, and 87 minutes, respectively, even when increasing the iron(III) concentration. The constant bromate ion reduction rate results because iron(III) reacts with hydrogen sulfide to form iron(II), and iron(II) reacts with bromate ion to reform iron(III). This cycle of reactions results in a constant (steady-state) bromate ion reduction rate.

It is important to note that although iron(III) decreases the rate of bromate ion reduction, the decrease of the reduction rate is small in the presence of $10^{-4}$ M H$_2$S and $10^{-5}$ M H$_2$S. Thus, some bromate ion will be reduced while it is retained in the stomach.

**Bromate Ion Reduction Confirmation with an LC-MS/MS**

The preliminary LC-MS/MS study was designed to verify the bromate ion half-life measured with an ion chromatograph and a LC-MS/MS. The bromate ion half-life was measured in two samples of 0.170 M HCl. Five bromate ion data points were measured during the eight hour study for each sample. The data were analyzed by comparing the bromate ion half-lives associated with each of the data points for each of the bromate ion samples.

The results of the LC-MS/MS preliminary study show that the measured bromate ion half-life in 0.170 M HCl ranges from 90 – 245 minutes. The average bromate ion half-life measured with the LC-MS/MS is 160 minutes. The average bromate ion half-life measured with an ion chromatograph is 153 minutes. Thus, there is acceptable agreement of the bromate ion half-life using both instruments. The standard deviation of the bromate ion half-lives measured by LC-MS/MS was 60 minutes, which was larger than was anticipated. The large standard deviation is most probably caused by experimental error. The development of a detailed LC-MS/MS protocol would eliminate many experimental errors, which would reduce the variance of the bromate ion measurements and improve the standard deviation.
Proof of Concept Bromate Ion Measurements with an ICP-MS

The ICP-MS could be used to verify the bromate ion measurements made with the ion chromatograph. The preliminary study was designed to determine if bromate ion could be measured accurately and reproducibly with an ICP-MS. The results of the preliminary ICP-MS experiments show that bromate ion standards and samples can be measured accurately and reproducibly in 0.017 and 0.0017 M HCl. The line equation and correlation coefficient for the bromate ion standards in the presence of 0.017 M HCl are $y = 0.941x + 9.827$ and 0.996, respectively. The line equation and correlation coefficient for the bromate ion standards in the presence of 0.0017 M HCl are $y = 0.995x + 1.297$ and 0.999, respectively.

Bromate ion samples of 256.0 µg/L and 250.0 µg/L were measured four times each in the presence of 0.017 M HCl and 0.0017 M HCl, respectively. The error of the 256.0 µg/L bromate ion samples in the presence of 0.017 M HCl is 11 %, and the error of the 250.0 µg/L bromate ion samples in the presence of 0.0017 M HCl is 13 %. The relative standard deviation of the 256.0 µg/L bromate ion samples in the presence of 0.017 M HCl is 5 %, and the error of the 250.0 µg/L bromate ion samples in the presence of 0.0017 M HCl is 6 %. The bromate ion calibration standard results are well within our expectations for preliminary experiments. The error and relative standard deviation results of the bromate ion samples are expected for a preliminary study. Improvement of the error and relative standard deviation of the bromate ion samples in the presence of hydrochloric acid solutions may be possible with the development of an improved ICP-MS protocol to measure bromate ion.

CONCLUSIONS

The objectives of this research project were to develop a method to measure bromate ion in hydrochloric acid with various reducing and/or oxidizing agents. The purpose of the measurements was to determine how rapidly bromate ion is removed in the stomach. The goal was to determine if ingestion of foods containing these oxidizing and/or reducing agents affects the rate of bromate ion loss. The final goal was to understand more about the chemical details of these bromate ion reactions.

A method, which included a new calibration curve for each solution or set of operating conditions, was developed in order to reduce the effects of bromate ion peak broadening in the
presence of high chloride ion solutions. This method was used to measure bromate ion reduction in synthetic gastric juice.

Initial bromate ion reduction rates were measured in the presence of various hydrogen ion and chloride ion solutions. The measured bromate ion half-lives ranged from 153 minutes in the presence of 0.170 M HCl to 30.2 days in the presence of 0.01 M H\(^+\) and 0.170 M Cl\(^-\). The results show that the rate of bromate ion reduction in the presence of only hydrochloric acid is too slow for a significant amount of bromate ion to be reduced while it is retained in the stomach.

The bromate ion reduction rate in the presence of hydrochloric acid and hydrogen sulfide significantly increases as compared to the presence of only hydrochloric acid. The bromate ion half-life in the presence of 0.170 M HCl is 153 minutes, while the bromate ion half-life in the presence of 0.170 M HCl and \(10^{-4}\) M H\(_2\)S is 2 minutes. Thus, the hydrogen sulfide in real gastric juice does significantly increase bromate ion reduction.

In response to the rapid bromate ion reduction rates in the presence of hydrogen sulfide, sulfite ion was studied as a “proof of concept” species. Sulfite ion is found in many wines at concentrations of 50 – 150 mg/L. The results indicate that sulfite ion significantly increases the rate of bromate ion reduction. The results in the presence of sulfite ion are comparable to the hydrogen sulfide results. Thus, sulfite ion concentrations typically found in one glass of wine would result in a bromate ion half-life in the stomach of less than 10 seconds.

The addition of the oxidizing agents, Cl\(_2\) or ClNH\(_2\) or iron(III), to synthetic gastric juice results in a decrease of the bromate ion reduction rate. The rate decreases because Cl\(_2\) and ClNH\(_2\) oxidize BrO\(_2\) or BrO\(_2^-\) to reform bromate ion and iron(III) reacts with hydrogen sulfide. Even though the rate decreases in the presence of these oxidizing agents, the ingestion of drinking water containing normal residual concentrations of approximately 0.1 – 2 mg/L of Cl\(_2\) or ClNH\(_2\) and the ingestion of foods containing as much as 10 mg/L of iron(III) should have little effect on bromate ion reduction in the stomach.

The addition of the reducing agents, iodide ion or nitrite ion or iron(II), to synthetic gastric juice results in an increase of the bromate ion reduction rate. The reducing agents increase the bromate ion reduction rate because they quickly remove bromate ion, BrO\(_2\), and BrO\(_2^-\) to minimize the regeneration of bromate ion. However, the ingestion of foods containing typical concentrations of iodide ion, nitrite ion, or iron(II) should have only a small effect on the rate of bromate ion reduction in the stomach.
In conclusion, the bromate ion reaction chemistry in the presence of hydrochloric acid and oxidizing or reducing agents has been described. The results can be used to help propose a more rigorous scientific methodology to determine low level toxicological effects for bromate ion.

**RECOMMENDATION FOR ADDITIONAL EXPERIMENTS**

The experiments reported here show that bromate ion reduction occurs in hydrochloric acid solutions of both oxidizing and reducing agents. However, there are still many additional experiments needed to totally understand the chemistry of bromate ion reduction in synthetic and real gastric juice.

The hydrogen ion, chloride ion, and hydrogen sulfide results have been used to develop an experimental rate law for the reduction of bromate ion in synthetic gastric juice. However, there are most probably many other reducing and oxidizing agents in real gastric juice that have not been identified. A detailed study of the oxidizing and reducing agents, as well as determining their concentration, in real gastric juice would help in the development of a detailed rate law for bromate ion reduction. This detailed rate law could be used to model the rate of bromate ion reduction for the general human population.

Bromate ion reduction was studied in the presence of some ingested oxidizing and reducing agents such as free available chlorine, monochloramine, ferrous and ferric iron, nitrite ion, and iodide ion. However, many additional studies are needed to determine the effect on the rate of bromate ion reduction for other chemicals, such as various foods and drinks. These studies are important because each of these components could have a significant effect on the rate of bromate ion reduction.

Measurement of bromate ion reduction in real gastric juice would be very beneficial for understanding the chemistry of bromate ion reduction. The gastric juice used for the bromate ion reduction studies should be taken from individuals with varying health conditions to determine the variance of the bromate ion reduction rate throughout the human population. The bromate ion reduction rate in real gastric juice could be used to compare with the bromate ion reduction rate using the experimental rate law.

These studies should give a better understanding of the bromate ion reduction chemistry, as well as help model the overall rate of bromate ion reduction in the stomach for the general human population.
REFERENCES


