INTERFERENCES IN AN AUTOMATED PHENOL RED METHOD FOR THE DETERMINATION OF BROMIDE IN WATER

by

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Abstract

The phenol red method for the determination of bromide in water has been automated using segmented flow analysis. Interferences to the determination have been characterized and compensations made. Samples studied include oil-field brines, halite-solution brines, groundwaters contaminated with these brines, and fresh groundwaters.

Samples can be analyzed at a rate of twenty per hour with a detection limit of 0.01 mg/L. The method is applicable up to 1.5 mg/L. The precision of the method ranges from approximately 1 to 8 % RSD (relative standard deviation) for diluted samples with concentrations from 1.1 to 0.14 mg/L bromide, respectively. Recovery studies for samples spiked with bromide gave an average recovery of 98.4 ± 4.9% with a range of 91.2 to 106%. Calibration curves, run in both ascending and descending order with respect to concentration, are approximately collinear with an average equation of peak height (arbitrary units) = (60.70 ± 0.34) $[Br^-]$ + (0.06 ± 0.25), with an SEE (standard error of estimate) = 0.46, and r (correlation coefficient) = 0.99991, over a range of 0.025 to 1.5 mg/L bromide.

Interferents were identified by spiking bromide standards with possible interfering substances. Chloride and bicarbonate cause significant positive interferences at concentrations as low as 100 mg/L and 50 mg/L, respectively.

Ammonia gives a negative interference that is important at levels as low as 0.05 mg/L. An ionic strength buffer is used to suppress a positive ionic strength interference, and correction curves are used to compensate for the chloride interference. The bicarbonate interference is minimized by acidification or can be compensated for with a correction curve, and the ammonia interference is eliminated by ion exchange. Chloride and ammonia interferences for the standard manual method were also characterized and similar procedures are effective for their removal or compensation. Studies of the products of the phenol red reaction are used to suggest a plausible mode of chloride interference. This interference is probably due to the formation of chlorinated phenol red products.

The automated phenol red method is superior to the standard manual method and has allowed better differentiation of the source(s) of salinity contaminating water resources.

For my wife, Kathy

May our love grow in every way,

with each passing day.

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I. INTRODUCTION

The concentration of bromide in freshwaters ranges from about 0.05 to 55 mg/L (1). In seawater, its concentration is 65 mg/L (2). It is also high in some formation brines, including oil-field brines, with values sometimes as high as several thousand mg/L (2). Halite- (naturally occurring sodium chloride) solution brines usually contain relatively small concentrations of bromide because they derive from the dissolution by freshwaters of natural halite deposits, which are very low in bromide.

The concentration ratio of bromide to chloride is indicative of the source of sodium chloride contamination of natural waters (3,4). At a given chloride concentration, this ratio is larger for oil-field brines or waters polluted by oil-field brines than it is for halite-solution brines or waters contaminated by halite-solution brines. A rapid, accurate method for the determination of bromide was needed for further study and application of this phenomenon.

Colorimetric methods were examined because they are well suited for automation by continuous flow techniques such as segmented flow analysis (SFA) or flow injection analysis (FIA). An SFA-automated method based on the catalytic effect of bromide on the oxidation of iodine to iodate by potassium permanganate in sulfuric acid solution (5) exhibits an unacceptable sensitivity to chloride (4,6,7) which precludes

its use with the saline samples of interest here. The standard phenol red method (8) indicated sufficient accuracy, precision, and sensitivity for our studies. This method has also been shown to be amenable to automation by SFA (9). A fluorescein method for bromide (10) that may have a low sensitivity to chloride and a low detection limit is presently being investigated elsewhere.

The latest edition of "Standard Methods for the Examination of Water and Wastewater" mentions that interferences to the phenol red method may be present in saline or polluted waters (8), but does not identify them. Various levels of chloride have repeatedly been stated not to interfere in the phenol red method (9,11,12), although one report (13) has warned of a possible interference, depending on reaction time and chloride concentration. Chloride was of major concern here because it may be found in high concentrations in oil-field brines, halite-solution brines, and freshwaters polluted with either of these.

Ammonia, which is often found in oil-field brines and sometimes in freshwaters, has been mentioned as an interference in the phenol red method (11,12,14), but no quantitative data have been published. Bicarbonate is often a major constituent in groundwaters. Reports of its tendency to interfere have been conflicting (11,13,15).

Other potential interferents are iodide (9,11,14), nitrite (14,15), ferric iron (15), and manganese (15). These

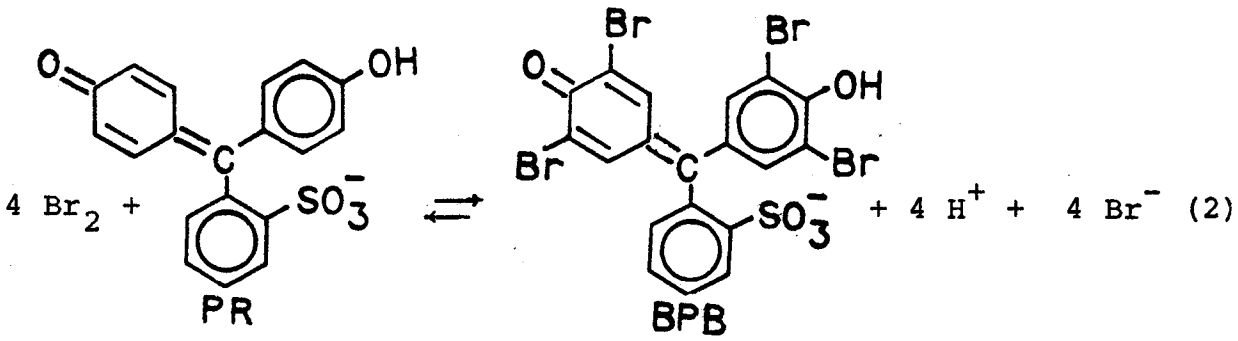
either exhibit negligible effects (7,15) or are normally found at such low concentrations in natural waters that they are not important to our studies.

In this thesis, the automation of the phenol red method by segmented flow analysis is described for the determination of bromide in natural waters. Preliminary interference studies were done using the manual method. Ionic strength, ammonia, chloride, and bicarbonate interferences are quantified and compensation procedures are presented for the automated method. Studies of the chemistry of the phenol red method to identify the actual products of the reaction and to characterize the mode of chloride interference are discussed. A comparison is made between the phenol red method, as modified in this work, and other standard methods for the determination of bromide. The effect on the ability to differentiate between salt pollution sources in natural waters due to the improvement of the phenol red method is also discussed.

II. BASIC CHEMISTRY OF THE PHENOL RED METHOD FOR BROMIDE DETERMINATION

The generally accepted reactions in the determination of bromide by the phenol red method are the oxidation of bromide to bromine by chloramine-T, followed by electrophilic substitution of the bromine onto phenol red (PR) to produce bromophenol blue (BPB):

$$H_3C{\cdot}C_6H_4{\cdot}SO_2NCl^- + 2\ H^+ + 2\ Br^- \rightleftharpoons H_3C{\cdot}C_6H_4{\cdot}SO_2NH_2 + Br_2 + Cl^- \quad (1)$$



Acetate buffer, phenol red, and chloramine-T solutions are added in sequence to an aliquot of the sample. After a set period of time, the absorbance of the reaction mixture is measured at 590 nm. The reactions are carried out at a pH of 4.6. At this pH, the solution containing the bromophenol blue formed is blue-purple, and the absorbance of the reaction mixture at 590 nm can be related to the bromide concentration in that sample. This is accomplished via a calibration curve prepared with bromide standards over the concentration range of interest.

III. PRINCIPLES OF SEGMENTED FLOW ANALYSIS

Segmented flow analysis (SFA) is one form of continuous flow analysis. The SFA system, used throughout this project, consists of several modules. These are, in the sequence in which they are utilized, an autosampler, proportioning pump, analytical cartridge, detector, and a recorder. Several publications cover the basic theory and operation of SFA systems (16-21). A brief summary is given here.

The autosampler utilizes an arm which holds a sample probe. The arm continually switches from a wash solution (usually water) to the sampling position and back. The rate at which this process occurs is controlled by a cam. The samples are contained in small plastic cups placed in a carousel which turns to a new sample position after the previous solution has been obtained.

The sample probe and reagent solutions are connected by tubes that lead to the proportioning peristaltic pump, which draws the sample, wash and reagent solutions into the system through pump tubing. The pump tubing diameters control the flow rates at which the sample or reagents are fed into the analytical cartridge.

The chemical reaction takes place in the analytical cartridge. Air bubbles are introduced into the sample stream (or a diluent stream into which the sample stream flows) at a regular interval, segmenting the sample stream into several small portions. This is accomplished by placing a pump tube,

which is open to the atmosphere at one end, in the pump. A bar squeezes shut a special silicone tube connected to this pump tube and opens the tube at two-second intervals, allowing the pump to draw air through the tube. The air is introduced into the flow stream through a special side-arm opening. The bubbles help mix the reaction mixture by promoting turbulent flow between bubbles. They also cleanse the system by scrubbing the tubing walls, thereby decreasing sample spread and memory.

Reagents are introduced by pumping them into the sample stream. The sequence and timing are set by their position of introduction along the tubing. A series of horizontal mixing coils is placed after each point of reagent introduction. These coils mix the sample and reagent solutions by allowing the more dense solution to fall continually through the less dense solution. If necessary, the flow stream can be sent through a heating bath.

The reaction mixture then flows into the detector. If necessary, the sample is debubbled before going into the flowcell. The solution in the cell is pumped to waste. Several detectors are available. These include a colorimeter, a spectrophotometer, an ion-selective electrode, a flame photometer, and a fluoronephelometer.

The signal is then recorded on a strip chart recorder and/or a digital printer.

IV. EXPERIMENTAL SECTION

Apparatus. A Beckman Model 25 spectrophotometer with a 1 cm sipper cell was used for the manual bromide determinations. Measurements of pH were made using either an Orion Model 801 Ionalyzer or a Sargent-Welch Model PBX pH meter, each using a combination pH electrode. A Technicon Auto-Analyzer II, consisting of an autosampler, proportioning pump, appropriate analytical cartridge, spectrophotometer, and strip chart recorder, was utilized for the automation of the phenol red method by SFA, the automated method interference studies, and the chloride and ammonia determinations. Spectra of reactants and products of the reaction were acquired on a Perkin-Elmer 555 UV-visible spectrophotometer.

Reagents. All reagents were analytical reagent grade, except for the chlorophenol red, which was indicator grade. Water for solution preparation and sample dilution was deionized and then distilled in an all-glass still.

The buffer, chloramine-T, and phenol red solutions were prepared as given in "Standard Methods" (8) for all the interference studies of the manual method, except for the bicarbonate interference. For the manual study of the bicarbonate interference, the final automated system reagents described below were used.

The following solutions were prepared for the final automated method. The phenol red solution was made by

dissolving 0.138 g of phenol red in 10 mL of water into which 0.4 mL of 1.0 N sodium hydroxide had been added, diluting to 1 L, and filtering through Whatman 40 filter paper. The chloramine-T reagent was prepared by dissolving 0.95 g of chloramine-T in water and diluting to 1 L. The ionic strength/pH 4.6 acetate buffer was made by adding 120.1 mL of glacial acetic acid and 2 mL of Brij-35 surfactant to a solution of 164.08 g sodium acetate, 127.52 g sodium nitrate, and 47.64 g magnesium sulfate in 700 mL of water and diluting to 1 L. A 6 M sodium nitrate solution was used to recharge the ion-exchange column. These solutions were used for all final interference characterization and elimination studies.

A "dilute" pH buffer that provides a reagent concentration in the flow stream similar to that in the manual method reaction mixture was used for the automated method interference identification studies and for preliminary automated method interference characterization studies. It was prepared by dissolving 20 mL of glacial acetic acid, 2 mL of Brij-35 surfactant, and 27.7 g of sodium acetate in water and diluting to 1 L.

The following solutions were prepared for the spectral studies. The buffer, chloramine-T, and phenol red used in the investigations of bromophenol blue, phenol red, and the phenol red reaction products were prepared as for the manual method (8). Studies of chlorophenol red and the chlorophenol red reaction product involved the phenol red and chloramine-T

solutions used in the final automated method plus the dilute pH buffer just described. The bromophenol blue solution was prepared by dissolving 0.409 g of bromophenol blue in 50 mL of water into which 6 mL of 0.1 N sodium hydroxide had been added, diluting to 1 L, and filtering. The chlorophenol red solution was prepared by dissolving 0.107 g of chlorophenol red in 20 mL of water into which 2.5 mL of 0.1 N sodium hydroxide had been added, diluting to 100 mL, and filtering.

The following stock solutions were prepared for the automated method interference studies: 100 mg/L ammonia from ammonium chloride, 10,000 mg/L chloride from sodium chloride (Ultrex), 1,000 mg/L bicarbonate from sodium bicarbonate, 700 mg/L sodium from sodium nitrate, 500 mg/L nitrate from sodium nitrate, 2,000 mg/L sulfate from sodium sulfate, 350 mg/L magnesium from magnesium sulfate, and 700 mg/L calcium from calcium nitrate tetrahydrate. In the manual method interference studies, a 1,000 mg/L sulfate solution from sodium sulfate and a 1,000 mg/L sodium nitrate solution were prepared in addition to the chloride, ammonia, and calcium solutions described above.

Bromide standards were freshly made as needed from a 500 mg/L bromide stock solution prepared from potassium bromide. Chloride and ammonia standards were prepared from the stock solutions.

Samples. Samples were collected in 1981 in accordance with established procedures (4).

General Procedure. Chloride and ammonia were determined by Technicon methods which use a modified Volhard procedure (22) and the Berthelot reaction (23), respectively. Argentometric titration was applied to determine chloride in oilfield brines. The procedures used to determine bromide were the standard manual method (8) for the manual interference studies and some of the spectral studies and the automated method as described below, or a manual method similar to the standard method (but with the same reagents and proportional volumes as used in the automated method) for the study of the cause of the bicarbonate interference and some of the spectral studies.

Two methods were used for standard additions of bromide or interferents, depending on convenience. The first method was pipeting the necessary volume of the spike into an undiluted volume of the solution of interest contained in a volumetric flask, and then diluting to the mark. The second was to pipet a very small volume of the spike into an aliquot of the solution of interest such that the volume addition was negligible compared to the total volume. Volume additions of less than or equal to 1.0 mL were made using micropipets.

For all repeated spiked-standard analyses the solutions were analyzed in ascending, descending, and random order with respect to bromide concentration to guard against misinterpretations due to carryover effects. The order for repeated sample analyses was varied each time the series of samples

was analyzed. Similarly, the order in which standards were analyzed was changed each time (ascending or descending). Standard bromide concentrations used were 1.5, 1.0, 0.5, 0.25, 0.1, 0.05, and sometimes 0.025 or 2.0 mg/L.

V. RESULTS AND DISCUSSION

A. Manual Method

1. Identification of interferents

Initial results by Whittemore (7) indicated that sodium nitrate, calcium, and sulfate do not interfere with the manual method, but that chloride does at concentrations near its maximum in freshwater or saline water samples diluted to bring the bromide concentration within the range of the method and/or to reduce the chloride interference. To confirm this, solutions of these substances were prepared at the same concentrations used by Whittemore. The bromide concentrations were then determined for these solutions and for the same solutions spiked with 0.5 mg/L bromide using the manual method (8) at room temperature (approximately 21° C). The bromide determinations were made at both 8 and 20 minutes because studies indicated that 8 minutes is a practical time to use for the automated method. The results are given in Table 1.

There is an important positive interference at 8 minutes for the sodium nitrate, sodium sulfate, calcium, and chloride solutions. Only chloride has an important positive interference at 20 minutes, which is only slightly greater than at 8 minutes. This strongly suggests that these interferences affect the rate of the reaction.

Table 1. Identification of Interferences to the Standard Manual Phenol Red Method

Possible Interferent[b]	Concentration, mg/L	Bromide mg/L added	Measured bromide, mg/L[a] 8 min	20 min
$NaNO_3$	1000	---	0.03	0.03
SO_4	1000	---	0.10	0.02
Ca	700	---	0.13	0.04
Cl	1000	---	0.16	0.07
$NaNO_3$	1000	0.50	0.52	0.50
SO_4	1000	0.50	0.57	0.50
Ca	700	0.50	0.62	0.50
Cl	1000	0.50	0.73	0.70
Blank (H_2O)	---	0.50	0.49	0.48
NH_3	0.5	---	NM[c]	<0
NH_3	0.5	0.50	NM	<0

[a]Unspiked values represent one measurement. Spiked values represent two measurements. Ammonia values represent one measurement.

[b]Charges are not indicated because there may be a variety of species present in solution due to complexation.

[c]Not measured.

Several samples of natural waters which were analyzed for bromide did not develop any blue-purple color. In fact, the signal was depressed below the blank. To determine if the interferent present was ammonia, samples which exhibited the interference, as well as those from the same geographical area that did not, were analyzed for ammonia. A definite correlation was found between samples which contained ammonia at concentrations greater than 0.1 mg/L (at the dilution used during the bromide determination) and those which showed a negative interference during the bromide determination. To verify that ammonia was the interferent, the bromide concentration was determined both for a solution of 0.5 mg/L ammonia as ammonium chloride, and a solution of 0.5 mg/L bromide spiked with 0.5 mg/L ammonia. This ammonia concentration was chosen because it is near the maximum value usually found in freshwater or the diluted saline water described above. The added ammonia caused a substantial negative interference at 20 minutes (Table 1).

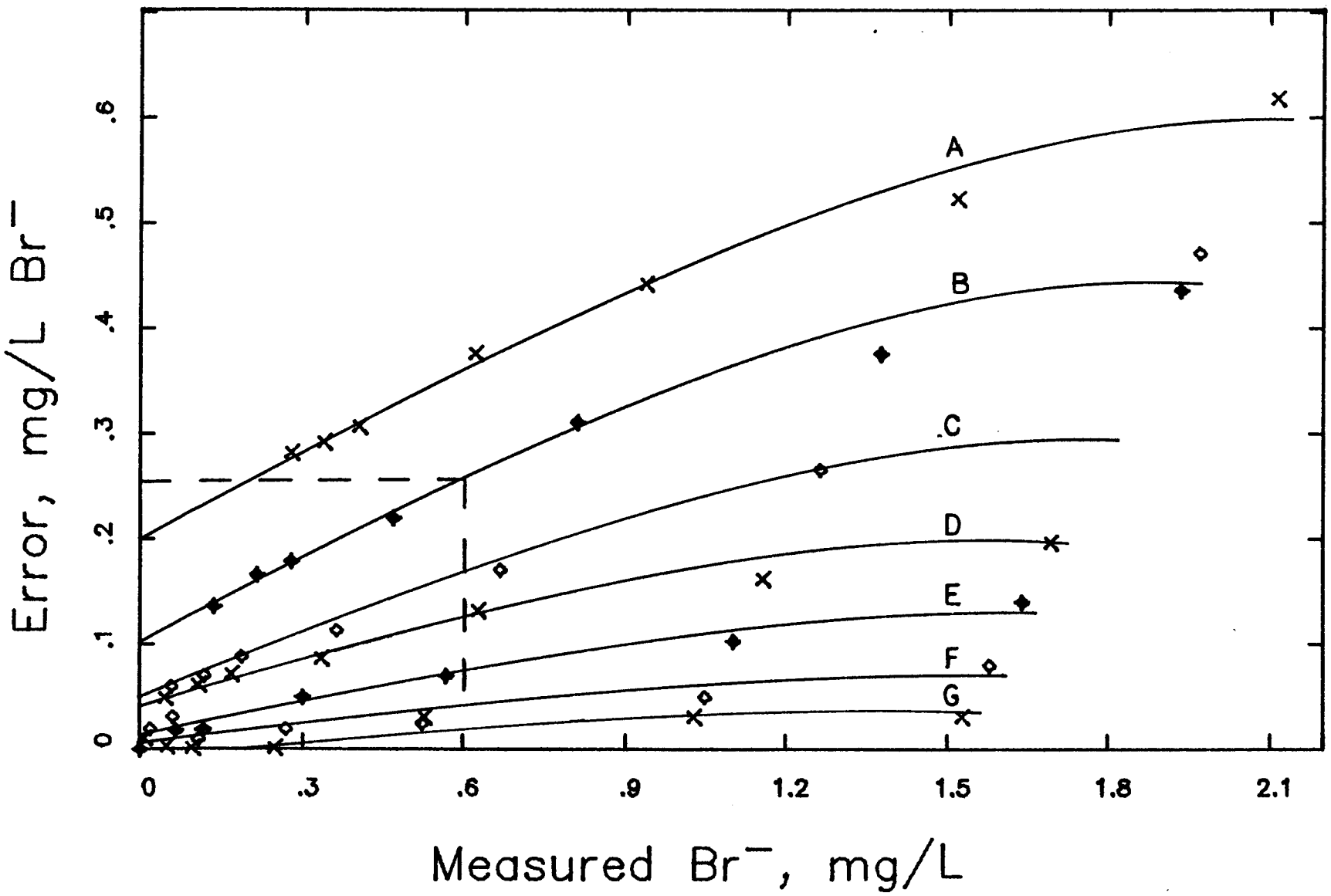
Therefore, the chloride and ammonia interferences were studied in more detail for the manual method.

2. Characterization and elimination of interferences

a. Chloride interference

A significant positive interference occurs for chloride levels as low as 50 mg/L (Figure 1). The curves in Figure 1 were obtained by adding known amounts of chloride to bromide

Figure 1. Error in the Manual Determination of Bromide Caused by Chloride: (A) 2000 mg/L; (B) 1000 mg/L; (C) 500 mg/L; (D) 200 mg/L; (E) 100 mg/L; (F) 50 mg/L; (G) 20 mg/L. Each point represents one measurement.


Error, mg/L Br⁻
0
.1
.2
.3
.4
.5
.6
0
.3
.6
.9
1.2
1.5
1.8
2.1
Measured Br⁻, mg/L
A
B
C
D
E
F
G

standards and measuring the bromide concentration, which is the sum of the actual bromide and the apparent bromide due to chloride. The actual bromide concentration in the solution is then subtracted from the measured bromide content to give the error (correction) due to chloride.

These curves can be used to correct for the chloride interference. The dissolved chloride and bromide in the sample are determined separately. The correction for the chloride concentration present is determined from a curve (or an interpolation between curves) at the measured bromide concentration. This correction is then subtracted from the measured bromide concentration to give the actual bromide content. For example (see Figure 1), the chloride correction for a sample with measured bromide and chloride concentrations of 0.60 mg/L and 1000 mg/L, respectively, would be 0.26 mg/L bromide, giving an actual bromide concentration of 0.34 mg/L. The effect of applying the correction to bromide standards spiked with chloride and to natural waters is shown in Table 2. The correction is accurate to within 8% for standards and is expected to give a similar accuracy for natural water samples.

A plot of apparent bromide versus chloride concentration due to chloride for chloride standards should not be used as a correction curve as it has been for the catalytic method (6), because the correction depends on both the chloride and the actual bromide concentrations. This may be more easily seen by replotting the data of Figure 1 as measured bromide versus

Table 2. Effect of Chloride Correction on the Manual Determination of Bromide in 0.50 mg/L Bromide Standards Spiked with Chloride and in Natural Waters

Chloride, mg/L in bromide standards	Measured bromide, mg/L[a,b]	
	Uncorrected	Corrected[c]
50	0.52	0.48
100	0.57	0.50
500	0.67	0.48
1000	0.81	0.54
2000	0.94	0.50

Sample[d]	Dilution[e]	Chloride mg/L[f]		
OFB1	3/500	149	0.71	0.60
SOFB2	1/50	554	0.80	0.58
HSB1	1/100	1930	0.48	0.16
SHSB2	15/100	1420	0.54	0.27
F1	none	63	0.06	0.04

[a]Values represent one measurement.

[b]Sample values represent concentration in diluted sample without removal of ammonia.

[c]Correction derived from data shown in Figure 1.

[d]OFB = oil-field brine; F = fresh groundwater; HSB = halite-solution brine; SOFB2 = saline water (fresh groundwater polluted with oil-field brine; SHSB2 = saline water (fresh water contaminated with halite-solution brine).

[e]Dilution of sample prior to bromide determination.

[f]Determined separately by method given in reference 22 or by argentometric titration.

chloride. Curves drawn through the points with the same actual bromide concentration exhibit increasing slopes for each increment in actual bromide. Changing the experimental conditions, especially the phenol red concentration, may eliminate this phenomenon (see Conclusions).

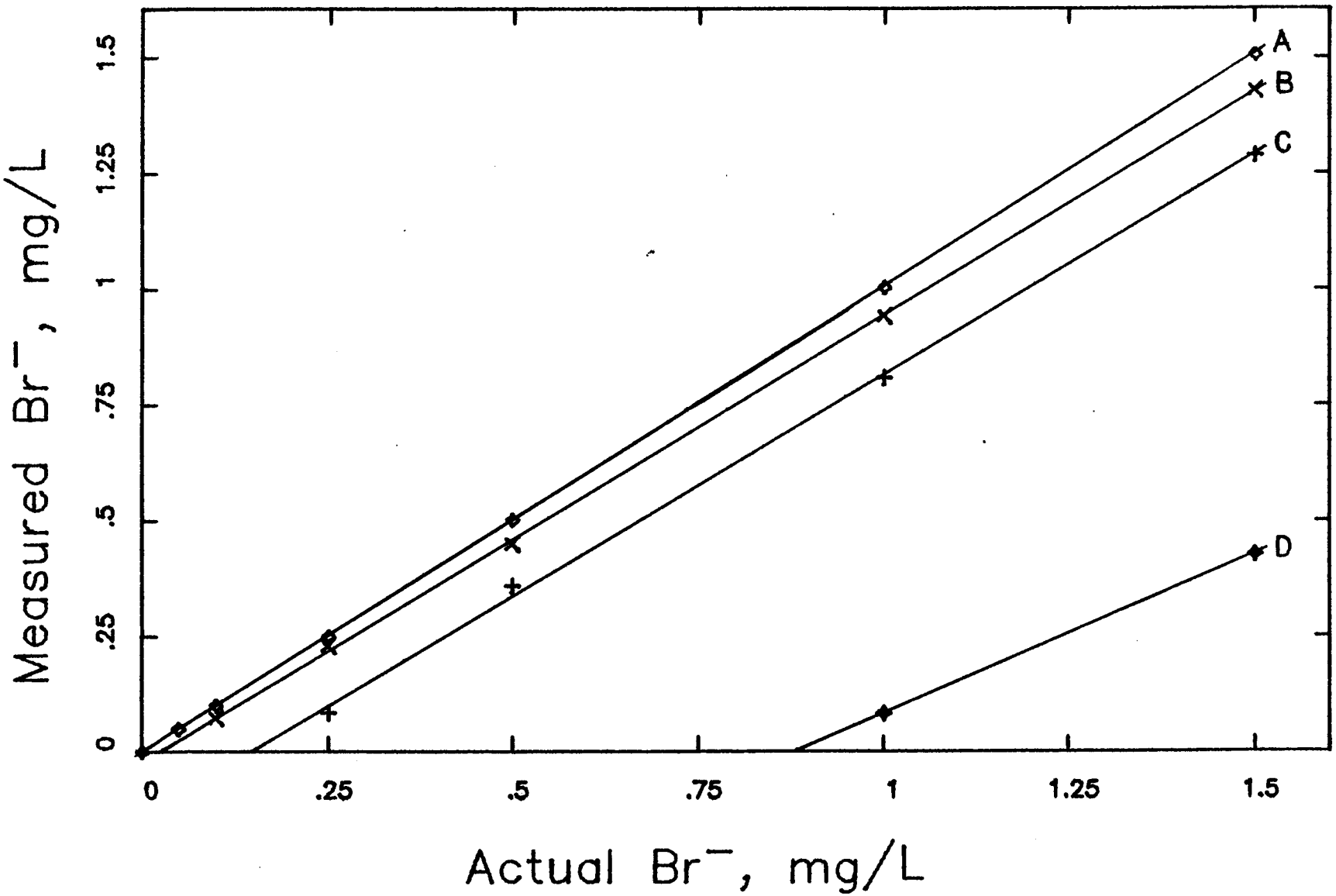
A set chloride level has been added to bromide standards for the determination of bromide in seawater (13). However, this would not give an accurate measurement here because the chloride varies greatly in groundwaters and surface waters. Controlling the ratio of phenol red to bromine (12) may effectively prevent the formation of halogenated products other than bromophenol blue, but this would be a tedious process. In addition, the specific qualitative and quantitative properties of the chloride correction curves may be different for other laboratories due to small instrumental and procedural variations. Therefore, curves should be generated by each lab using them.

b. Ammonia interference

A significant negative interference occurs for ammonia levels as low as 0.05 mg/L. Curves showing the extent of the ammonia interference (Figure 2) were obtained by adding known amounts of ammonia to bromide standards and measuring the bromide concentration.

At the reaction pH of 4.6, most of the ammonia is in the form of ammonium ion. This does not eliminate the possibility that ammonia is an interfering species, but strongly suggests

Figure 2. Effect of Ammonia on the Manual Determination of Bromide: (A) 0.0 mg/L; (B) 0.05 mg/L; (C) 0.1 mg/L; (D) 0.5 mg/L. Concentrations of 1.0 and 2.0 mg/L ammonia gave readings below the blank for all bromide concentrations (0.05 to 1.5 mg/L). Each point represents one measurement.


Measured Br⁻, mg/L
0
.25
.5
.75
1
1.25
1.5
Actual Br⁻, mg/L
A
B
C
D

that the ammonium ion is. If ammonia is the interfering species, it would be consumed in the interfering reaction. Then, more would be formed by dissociation of the dissolved ammonium. Regardless, this interferent is referred to as ammonia as a more general term and should be considered to include organic amines which would conceivably interfere similarly.

The ammonia interference may be caused by a decrease in oxidant and/or brominating species concentration during the formation of chloramines, bromamines, and/or nitrogen by the reduction of hypochlorite (11), bromine, or any hypobromite (24) formed in the reaction. It is unlikely that halamines react in the phenol red method in a manner similar to bromide as has been suggested (15) because signals for standards with ammonia-to-bromide ratios of approximately one are depressed below the blank. This indicates a decreased formation of halogenated phenol red products.

Several samples of groundwaters which were not refrigerated after collection, but were placed in the back of a vehicle for transportation on a hot day, exhibited no ammonia interference. Later, after the same waters were sampled again but were immediately refrigerated, they exhibited an ammonia interference. This phenomenon was probably due to an increase in pH from the loss of carbon dioxide in the warm, unrefrigerated samples. At the higher pH, some dissolved ammonium ion was converted to ammonia, which then volatilized. The pH of many groundwaters may increase to as high as 9.0

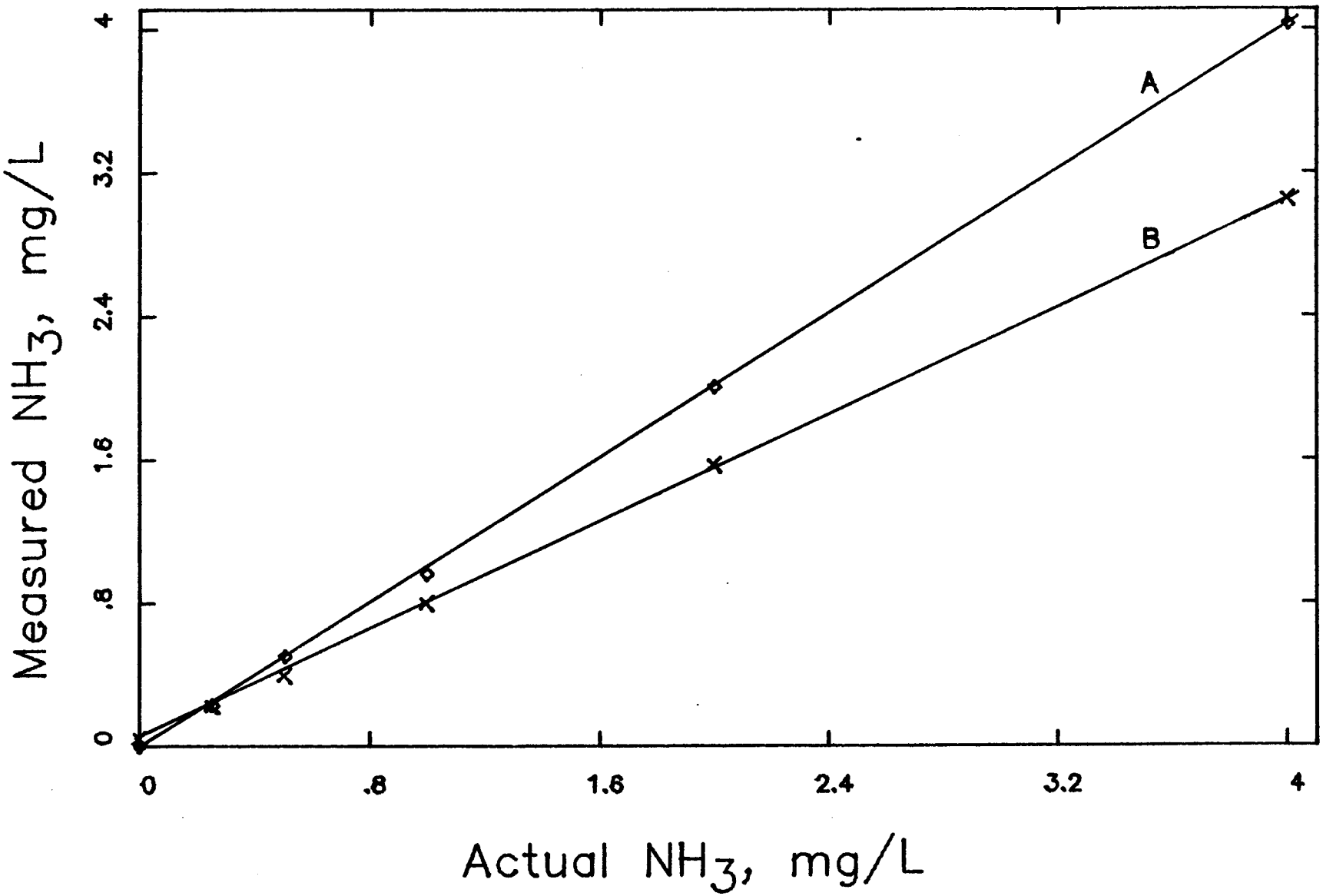
from the loss of dissolved carbon dioxide after sampling. This is near the pKa of ammonia; thus, given the solubility of ammonia at this temperature, as much as one-half of the ammonia could be lost. Some ammonia may have been adsorbed on the container walls also.

This process was simulated in the laboratory by heating samples, bromide standards, and bromide standards spiked with known amounts of ammonia for about 15 hours in a water bath at approximately 40° C. The heated bromide standards were used to prepare a calibration curve so any bromide lost as bromine would be compensated for. Comparison of the absorbance found for heated standards with unheated standards indicated some bromide was lost due to heating. Volume loss due to evaporation was corrected by addition of water.

The process did not work well for the standards spiked with ammonia. This may be due to the absence of dissolved carbonate species in these solutions so the pH would not increase upon heating. Addition of base could eliminate this problem by increasing the formation of ammonia. The measured bromide concentration increased for the samples, indicating the loss of some ammonia.

To verify the loss of ammonia from the solutions, ammonia standards were prepared, adjusted to a pH of approximately 9.0, heated as above, and the remaining ammonia concentration was measured (Figure 3). Unheated ammonia standards were used to prepare a calibration curve. Ammonia removal does occur,

Figure 3. Effect of Solution Heating on the Determination of Ammonia in Ammonia Standards Adjusted to pH 9.0.
(A) Unheated ammonia standards;
(B) Heated ammonia standards.
Each point represents an average of two measurements.


Measured NH_3, mg/L
Actual NH_3, mg/L
0
.8
1.6
2.4
3.2
4
A
B

but is far from complete as expected from the pKa and solubility of ammonia. However, the pH of the solutions decreased during heating, perhaps due to dissolution of silica in the glass or reaction with atmospheric carbon dioxide. This decreased the efficiency of the removal process. It is probably more efficient for natural water samples in which the pH would increase.

Because the solution heating process was inefficient and time-consuming, a different method of ammonia removal was devised. Adding an ammonia "buffer" which would make any variations in ammonia concentration in most natural water samples negligible compared to that already in the reaction mixture cannot be used because this would decrease the bromide signal. Ion exchange has been reported to be an efficient method of ammonia removal (24). An ion-exchange column was prepared by filling a 50 mL buret plugged with glass wool approximately half full with a slurry of Dowex 50WX8 cation exchange resin in water.

The column was first used with hydrogen ion on the exchange sites. Interfering ammonia levels were removed relatively completely from bromide standards spiked with ammonia. However, if samples with high dissolved solids were run through the column and exchange of all cations was fairly complete, the sample pH would decrease greatly. This would interfere with the phenol red reaction which is buffered at pH 4.6. Thus, a column with sodium ion on the exchange sites was prepared.

The column was first charged with 6 M sodium nitrate and then rinsed with 300 mL of water. A 50 mL aliquot of a standard or sample was passed through the column at a rate of 5 mL per minute and collected in a 100 mL volumetric flask. An additional 50 mL of water was run through the column and collected in the same flask and was brought to volume with water, if necessary. Between each sample or standard, approximately 100 mL water was passed through the column and discarded. After every two to three samples or standards, the column was recharged with 25 mL of 6 M sodium nitrate at a rate of 2.5 mL per minute. After recharging, the column was rinsed with approximately 300 mL of water.

A series of bromide standards, bromide standards spiked with ammonia, and water samples were treated using the sodium-saturated column and then analyzed for bromide and ammonia. The ammonia removal was essentially complete and a corresponding increase in measured bromide concentration was found in all cases (Table 3).

B. Automated System

1. System development

Two publications which outline the basics of automation by segmented flow analysis (SFA) were used as guidelines to automate the phenol red method (17,25). The reagent and sample pump tube diameters (flow rates) and reagent concentrations were chosen such that the reagent and sample concentrations in the flow stream were similar to those in the reaction

Table 3. Effect of Manual Ion Exchange on the Manual Determination of Bromide in Bromide Standards Spiked with 0.5 mg/L Ammonia and in Natural Waters.

	Measured concentrations, mg/L[a,b]			
	Without ion exchange		With ion exchange	
Bromide, mg/L in standard	Ammonia	Bromide	Ammonia	Bromide
0.00	NM[c]	<0[d]	0.00	0.01
0.25	NM	<0	0.01	0.24
0.50	NM	<0	0.00	0.50
1.00	NM	0.08	0.00	1.00
Sample[e]				
F2	0.47	<0	0.01	0.14
F3	0.39	<0	0.00	0.36
F4	0.73	<0	0.00	0.37

[a]Values represent one measurement.

[b]Bromide values are corrected for chloride interference.

[c]Not measured.

[d]Signal below blank.

[e]F = Fresh groundwater.

mixture of the manual method (8). In the first automated configuration of the phenol red method, the reagent concentrations were the same as those in the manual method, except for the chloramine-T solution, which was one-fourth of the concentration in the manual method. Two mL/L of Brij-35 surfactant were added to the buffer. The thiosulfate solution used to stop the reaction in the manual method was not used since the reaction timing is controlled automatically. The pump tube flow rates used were as follows: sample, 2.5 mL/min; reagents, 0.1 mL/min; waste, 1.6 mL/min; air, 0.32 mL/min; wash water, 2.9 mL/min.

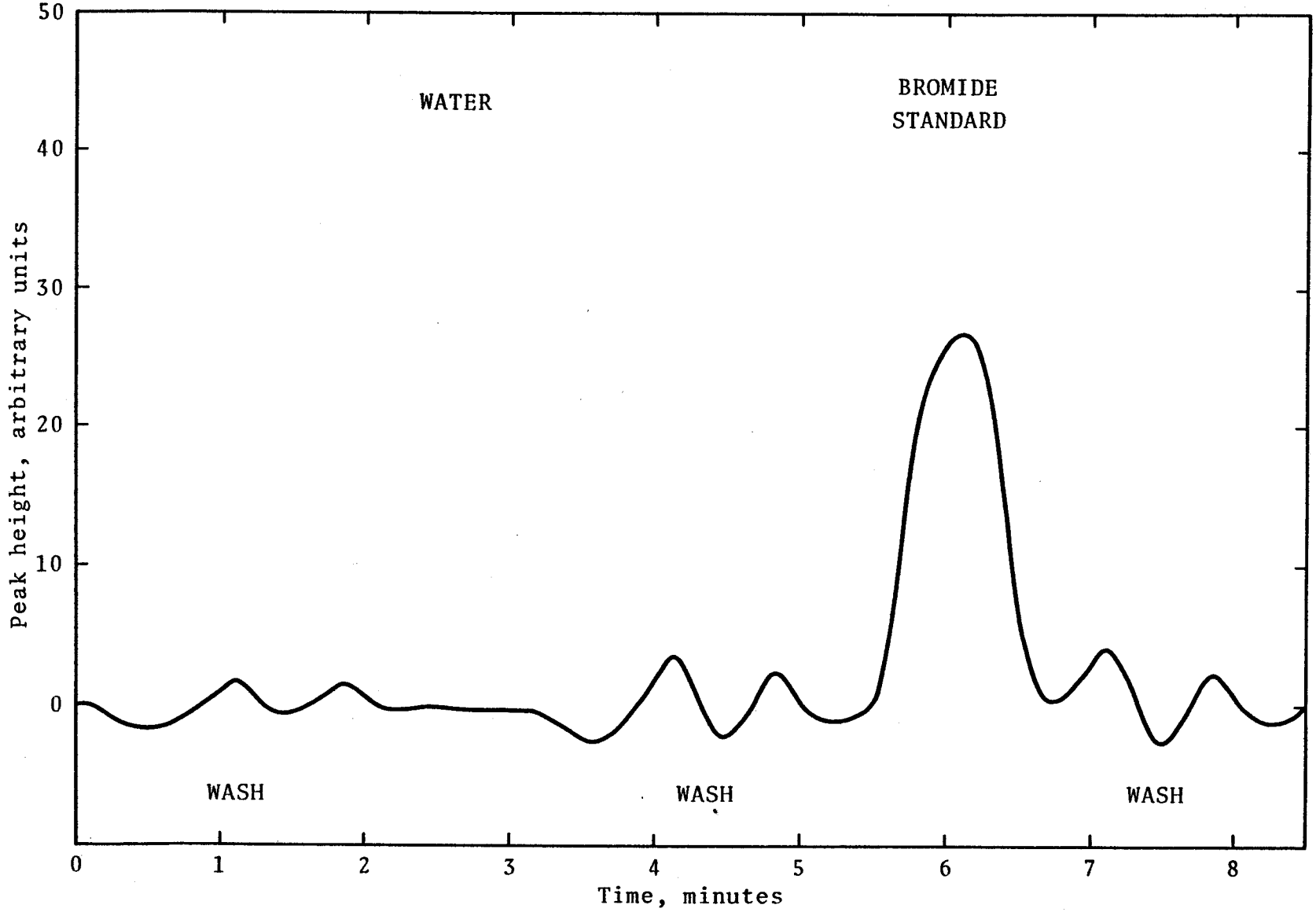
The segmenting bubbles were introduced into the sample as it was pumped into the system. Next, buffer, phenol red, and chloramine-T solutions were introduced in sequence and mixed by 5 or 10 turn coils. After the chloramine-T introduction, the solution passed through an additional coil (Fisher Scientific #105-1173-010) with an equivalent length of 12.2 m. This coil was chosen because it delayed the measurement by approximately 20 minutes, the reaction time used in the manual method (8). The solution was then debubbled and entered the spectrophotometer flowcell, which has a 1.5 cm pathlength, where the absorbance was measured at 590 nm with an 8 nm bandpass.

Two groups of problems arose with this system. The first problem was caused by the intersample bubbles, drawn into the system when the autosampler changed from the wash to the

sample position, and vice versa. This bubble is small enough, in published automated methods, that it is removed by the flow-cell debubbler with the large bubbles introduced to produce segmented flow, or before the stream reaches the flowcell debubbler if another debubbler is included in the system. However, in this method the intersample bubble was unusually large because the flow rate of the sample pump tube was greater than in most methods. Thus, the intersample bubble was not completely removed by the flowcell debubbler. This caused the recorder to go off-scale in the positive direction both before and after sample peaks, often obscuring the peak completely. To remedy this, a debubbler (Technicon #116-0200-P02) was placed on the sample line immediately after the pump and immediately before the bubble injector. The pump tube used with the debubbler was 0.42 mL/min, so the sample pump tube was increased to 2.9 mL/min to maintain approximately the same reagent/sample mixture.

However, a periodic oscillation remained on the baseline after insertion of the debubbler (Figure 4). This oscillation was still present when the reaction time was shortened to 8 minutes, but was not present when the sampler was not in operation. The oscillation was caused by compression of the intersample air bubble. As an intersample bubble goes through the pump, the space it occupies increases (25). This probably causes more of the sample or blank solution to be injected into the flow stream at the bubble injection fitting. When leaving the pump, the bubble compresses to occupy its

Figure 4. Periodic Oscillation on Baseline of Strip Chart Readout for Automated Phenol Red Method for the Determination of Bromide without Prepump Debubbler.


50
40
30
20
10
0
Peak height, arbitrary units
WATER
BROMIDE
STANDARD
WASH
WASH
WASH
0
1
2
3
4
5
6
7
8
Time, minutes

original volume. As this happens, less sample (or water blank) is injected into the flow stream at the bubble injection fitting (25). Because the blank absorbs at the same wavelength as the bromide reaction product (see later discussion), a difference in absorbance along the baseline will be seen. This is because changing amounts of water are introduced into the flow stream diluting the reaction mixture (and, therefore, the absorbing species) by a different value.

This problem was eliminated in the final automated configuration (8 minute reaction time) by placing a T-connector (# 115-B034-01, used to introduce solutions into the flowing stream) between the debubbler and the bubble injection fittings. A 0.05 mg/L pump tube was attached to the T-connector and a solution of 4 mL/L Brij-35 surfactant was pumped in. The surfactant facilitated even injection of the sample into the flow stream and eliminated the baseline waveform. Unfortunately, for some unknown reason, this provided only a temporary solution and a few weeks later the baseline waveform reappeared. Placing the debubbler before the pump provided a permanent solution to the intersample air compression problem (6) since the intersample air bubble never reaches the pump.

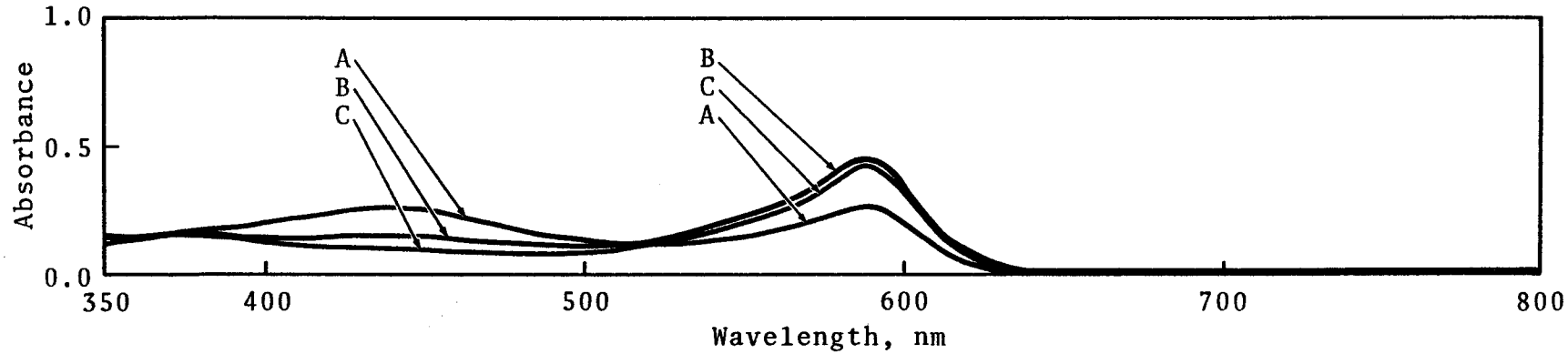
The second group of problems was related to the long reaction time (20 minutes). Most automated methods involve reaction periods of only a few to several minutes after mixing of samples and reagents. The longer time was both inconvenient for operations such as zeroing the spectrophotometer

with the blank and undesirable due to carryover between samples. Thus, the rate of color development in the phenol red method was investigated to determine whether a shorter reaction time could be used. A Perkin-Elmer Model 555 Spectrophotometer was used to scan reaction mixtures of blanks and bromide standards (Figure 5) prepared using the standard method. One minute elapsed between the chloramine-T addition and the beginning of the scan.

The maximum net absorbance at 590 nm is almost obtained in ten minutes. This was found by subtracting the corresponding absorbance values for the blank reaction mixture from the 0.5 mg/L bromide reaction mixture at each time shown in Figure 5. The net absorbance will go up slightly after this time, but after roughly 12 minutes the actual absorbance begins to drop. The actual time at which the fading begins was found to be longer in some cases, but at 8 minutes the actual absorbance is always near the maximum. Others have noted this drop in absorbance (12,26,27). The major product of this reaction, bromophenol blue, fades with time in alkaline medium (28,29) due to formation of an unconjugated form of bromophenol blue. Formation of the unconjugated bromophenol blue may be the cause of the fading seen in this study, but it is probably not formed to a very great extent since the pH is buffered at 4.6.

This indicator fading occurs much more rapidly at bromide concentrations greater than 1.5 mg/L, a phenomenon noted

Figure 5. Change in Absorbance of the Phenol Red Reaction Mixture with Time for 0.5 mg/L Bromide. Time at 590 nm: (A) 2 min 46 s; (B) 8 min 46 s; (C) 14 min 46 s. Instrument settings are given in Appendix A.


1.0
0.5
0.0
Absorbance
A
B
C
B
C
A
350
400
500
600
700
800
Wavelength, nm

by others (12,14,27). The absorbance rises very rapidly, and then drops off rapidly. This is a disadvantage of the automated method because samples which are high in bromide concentration may appear to have a very low concentration.

Eight minutes was a convenient delay time to change to, since longer delay times, which were conveniently obtained by adding coils, made it difficult to zero the spectrophotometer when the blank solution was being measured. Using the eight-minute reaction time somewhat reduces the problem of the rate increase due to high bromide concentrations.

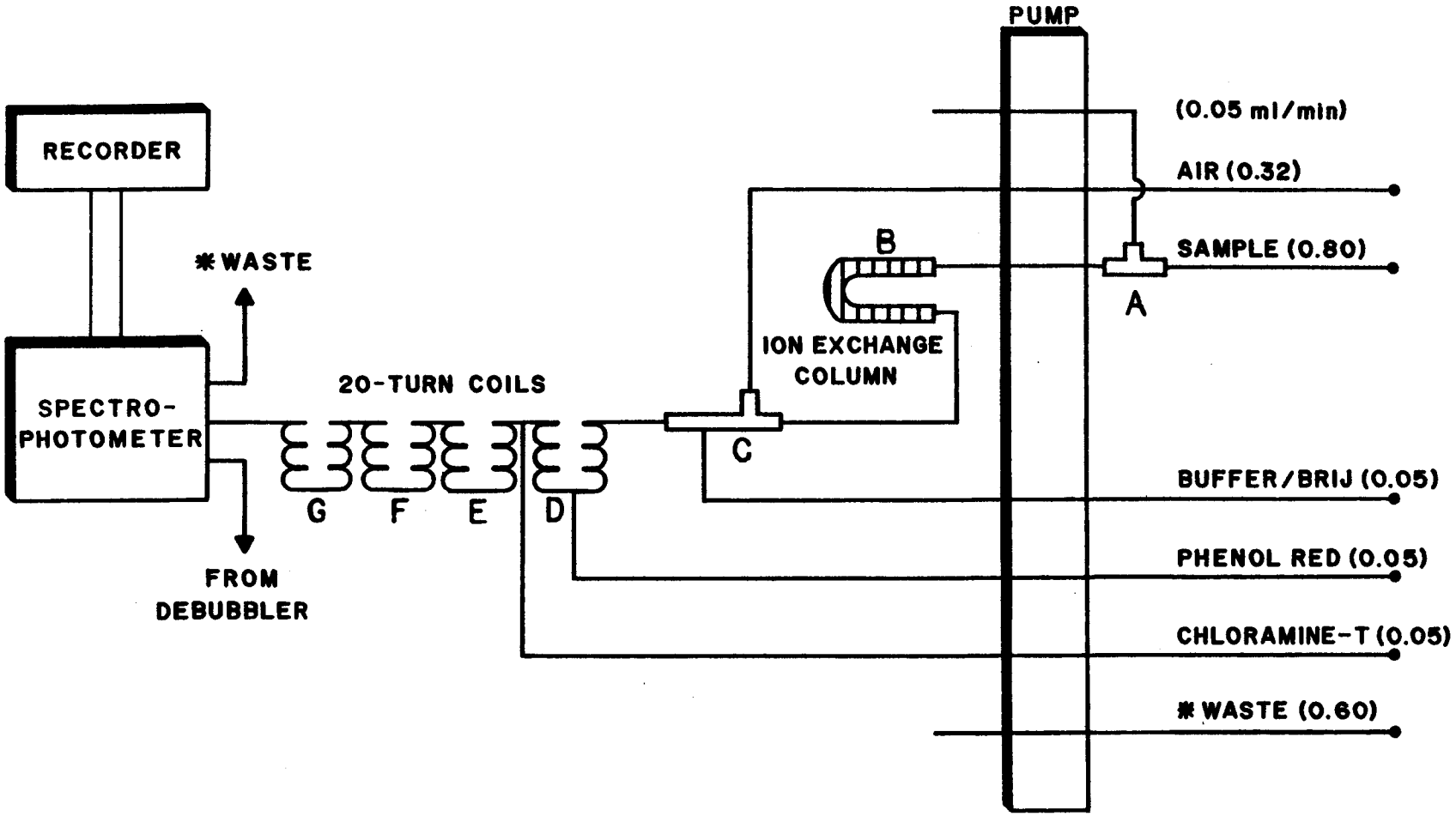
In order to reduce the reaction time to approximately eight minutes, the mixing and delay coils were replaced with a series of four 20-turn mixing coils. The reagent pump tubes were changed to 0.03 mL/min, the sample and wash-water pump tubes were both changed to 0.80 mL/min, and the waste pump tube was changed to 0.6 mL/min. The reagent concentrations were changed so their concentration in the flow stream remained similar to that in the manual method reaction mixture. The buffer and phenol red are each mixed into the sample stream by flowing through 10 turns of coil. After the chloramine-T introduction, the solution is further mixed and delayed by eight minutes before entering the flowcell.

Attempts to increase the detection limit by using a 5 cm flowcell, instead of the 1.5 cm flowcell, failed because the blank absorbed too strongly to zero the spectrophotometer.

The final system is shown in Figure 6. To increase the accuracy of the reagent introduction flow rates, the reagent

Figure 6. Schematic Diagram of Final Segmented Flow Analysis System for Determination of Bromide Using the Phenol Red Method. Item numbers are for Technicon Instruments Corporation parts.

A.	T-connector (debubbler)	#116-0200-P02
B.	Ion-exchange column	#189-0000-01
C.	Injection fitting	#116-0489-01
D.	Manifold coil	#157-B089-01
E.	Manifold coil	#157-B095-01
F.	Manifold coil	#157-0248-01
G.	Manifold coil	#157-0248-01


PUMP
RECORDER
(0.05 ml/min)
AIR (0.32)
SAMPLE (0.80)
*WASTE
B
A
ION EXCHANGE
COLUMN
20-TURN COILS
SPECTRO-
PHOTOMETER
C
G
F
E
D
BUFFER/BRIJ (0.05)
PHENOL RED (0.05)
CHLORAMINE-T (0.05)
FROM
DEBUBBLER
*WASTE (0.60)

concentrations were again chosen so that their concentrations in the flow stream were similar to those in the manual method reaction mixture. However, the buffer was increased in capacity and ionic strength to minimize interferences due to the wide ranges of buffer capacities and ionic strengths of the samples, as described later. A 20-per-hour adjustable cam was modified to increase the wash cycle time by cutting off one section of both sample positions of one of the metal plates--the other plate was not used. The final sample-to-wash time ratio was 1.25:1. This reduces carryover. The water wash pump tube used was 0.80 mL/min.

The sample is first pumped into the debubbler. Next, the sample enters an ion-exchange column to remove any ammonium ion. The column was constructed by filling a column (Technicon #189-0000-01) with water, slowly adding Dowex 50WX8 cation exchange resin with tapping, and plugging the ends with glass wool. After the column, the segmenting bubbles are introduced with an injection fitting. Next, buffer, phenol red, and chloramine-T solutions are introduced in the usual sequence and mixed by passing through coils. Following the chloramine-T introduction, additional coils delay the absorbance by eight minutes. The solution is then debubbled and enters the spectrophotometer flowcell (pathlength = 1.5 cm) where the absorbance is measured at 590 nm with an 8 nm bandpass.

The recorder is zeroed with the sampler in the wash cycle. The highest standard is then sampled several times to set

full scale. A series of standards is placed first on the sample carousel, followed by samples with water interspersed every seven to eight samples. Approximately every hour, the ion-exchange column is recharged by sampling two aliquots of the 6 M sodium nitrate solution. The highly concentrated sodium nitrate solution causes a severe negative interference, perhaps due to an impurity. Therefore, two aliquots of water are sampled immediately before and after the sodium nitrate. A series of standards is run at approximately 1.5 hour intervals.

2. System characterization

Eighteen sets of bromide standards were run in both ascending and descending order with respect to concentration. The calibration curves are approximately collinear with an average equation of peak height (arbitrary units) = (60.70 ± 0.34) $[Br^-]$ + (0.06 ± 0.25), with an SEE (standard error of estimate) = 0.46, and r (correlation coefficient) = 0.99991, over a range of 0.25 to 1.5 mg/L bromide. A slight concavity upwards was noted for some of the curves at bromide concentrations less than approximately 0.2 mg/L.

The detection limit, defined as that concentration giving a signal equal to three times the standard deviation of the blank determinations, is 0.01 mg/L. The standard deviation was obtained from 10 peak heights for the 0.025 mg/L standard, assuming that there would be no change in noise from the blank. Therefore, the phenol red method is suitable for the

determination of bromide in most groundwaters and surface waters. The throughput is 20 samples per hour.

Precision was measured by determining the bromine concentration of each of 26 samples nine times during a four-day period. The data are tabulated in Appendix B. These samples consisted of oil-field brines, halite-solution brines, fresh groundwaters, and groundwaters polluted with oil-field or halite-solution brines with bromide concentrations ranging from 0.14 to 1.1 mg/L, after any necessary dilution. Percent relative standard deviations (% RSD) ranged from approximately 1% at the higher concentration to 8% at the lower concentration. Several samples had % RSD values higher than those expected for their bromide concentration. These samples were all in nearly empty bottles, and it is believed that the high % RSD values may have resulted from dried inorganic salts on the bottle lip dissolving in different amounts each time the sample was poured out for analysis.

An indication of the accuracy of the method was obtained by spiking 10 samples with 0.125 or 0.25 mg/L Br. The data are tabulated in Appendix C. The samples consisted of oil-field brines, halite-solution brines, fresh groundwaters, and waters polluted with oil-field or halite-solution brines. The bromide concentrations ranged from approximately 0.15 to 1.0 mg/L. The average recovery was 98.4 $\pm$ 4.9% with a range of 91.2 to 106%.

3. Identification of interferents

To identify potentially serious interferences, bromide concentrations were repeatedly determined for solutions, both unspiked and spiked with 0.5 mg/L bromide, that contained the common major cations and anions found in fresh and/or saline waters. The major constituent concentrations used are near the maximum found in freshwaters or saline waters diluted to bring the bromide concentration within the range of the method and/or to reduce the chloride interference. The results for the spiked solutions are given in Table 4.

Use of the dilute pH buffer gave a positive interference for all major constituents added except ammonia which, as expected, gave a serious negative interference.

A relatively linear relationship was found between the concentration of each specific ion and the measured bromide concentration. However, a mode of interference intrinsic to each specific ion seemed improbable. Ionic strength also gave a fairly linear relationship with measured bromide, as shown in Figure 7. A different ionic strength could conceivably change the measured bromide concentration (sum of apparent plus actual bromide) due to kinetic effects (30,31), especially since these interferences appear to affect the rate of the phenol red reaction, as discussed in the manual method section.

As discussed in the next section, use of an ionic strength/

Table 4. Effect of Major Constituents of Natural Waters on the Determination of Bromide (0.50 mg/L) by the Automated Phenol Red Method.

Constituent	Conc., mg/L	Measured bromide, mg/L[a]	
		Dilute pH buffer[b]	Ionic strength/ pH buffer[b]
Na	700	0.61	0.49
NO_3	500	0.53	0.49
Mg	350	0.60	0.49
SO_4	1500	0.65	0.48
Ca	700	0.62	0.49
Cl	1000	0.87	0.58
HCO_3	1000	>1.50[c]	1.08
NH_3	0.1	0.37[d]	0.43[d]

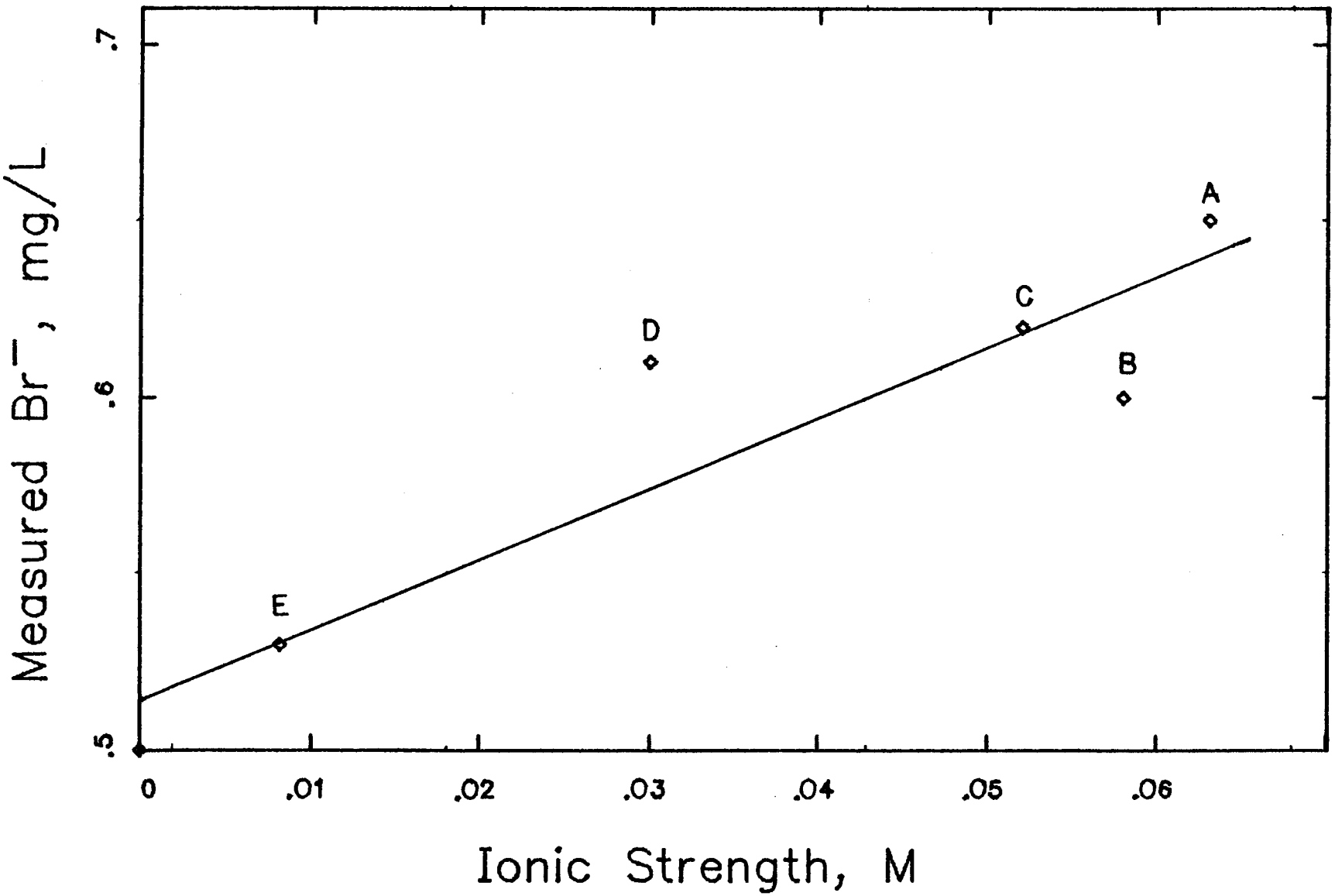
[a]Values represent an average of three measurements.

[b]See Experimental section for composition.

[c]Off-scale.

[d]These values were determined with the ion-exchange column removed.

Figure 7. Effect of Ionic Strength on the Automated Determination of 0.5 mg/L Bromide: (A) 2000 mg/L sulfate as sodium sulfate; (B) 350 mg/L magnesium as magnesium sulfate; (C) 700 mg/L calcium as calcium nitrate; (D) 700 mg/L sodium as sodium nitrate; (E) 500 mg/L nitrate as sodium nitrate. Each point represents an average of three measurements.


Measured Br⁻, mg/L
.7
.6
.5
A
B
C
D
E
0
.01
.02
.03
.04
.05
.06
Ionic Strength, M

pH buffer eliminated all positive interferences except chloride and bicarbonate. Therefore, ionic strength, ammonia, chloride, and bicarbonate were selected for further, more detailed studies.

4. Characterization and elimination of interferences

a. Ionic strength interference

As shown in the manual method section, a longer reaction time may eliminate the ionic strength interference, but it has deleterious effects as discussed in the automated method development section. An ionic strength buffer was used to eliminate this interference (31). The buffer increases the ionic strength of the reaction mixture appreciably enough to make the ionic strength introduced by natural waters negligible. For simplicity, the ionic strength and pH buffers were prepared as one solution.

To develop a suitable ionic strength/pH buffer, several different buffers were prepared. The solutions described in the preceding section were each analyzed for bromide using these buffers to determine the best one for eliminating the ionic strength interference. These buffers all contained acetate buffer (an acetic acid-sodium acetate mixture) with pH buffering capacities higher than that of the dilute pH buffer to reduce the bicarbonate interference, as discussed later. Some of the buffers consisted only of the acetate buffer in different concentrations. For others, sodium nitrate was added to the acetate buffer, or both sodium

nitrate and magnesium sulfate were added. The ionic strength of these solutions ranged from 2.1 to 5.5 M, without considering ion pairing.

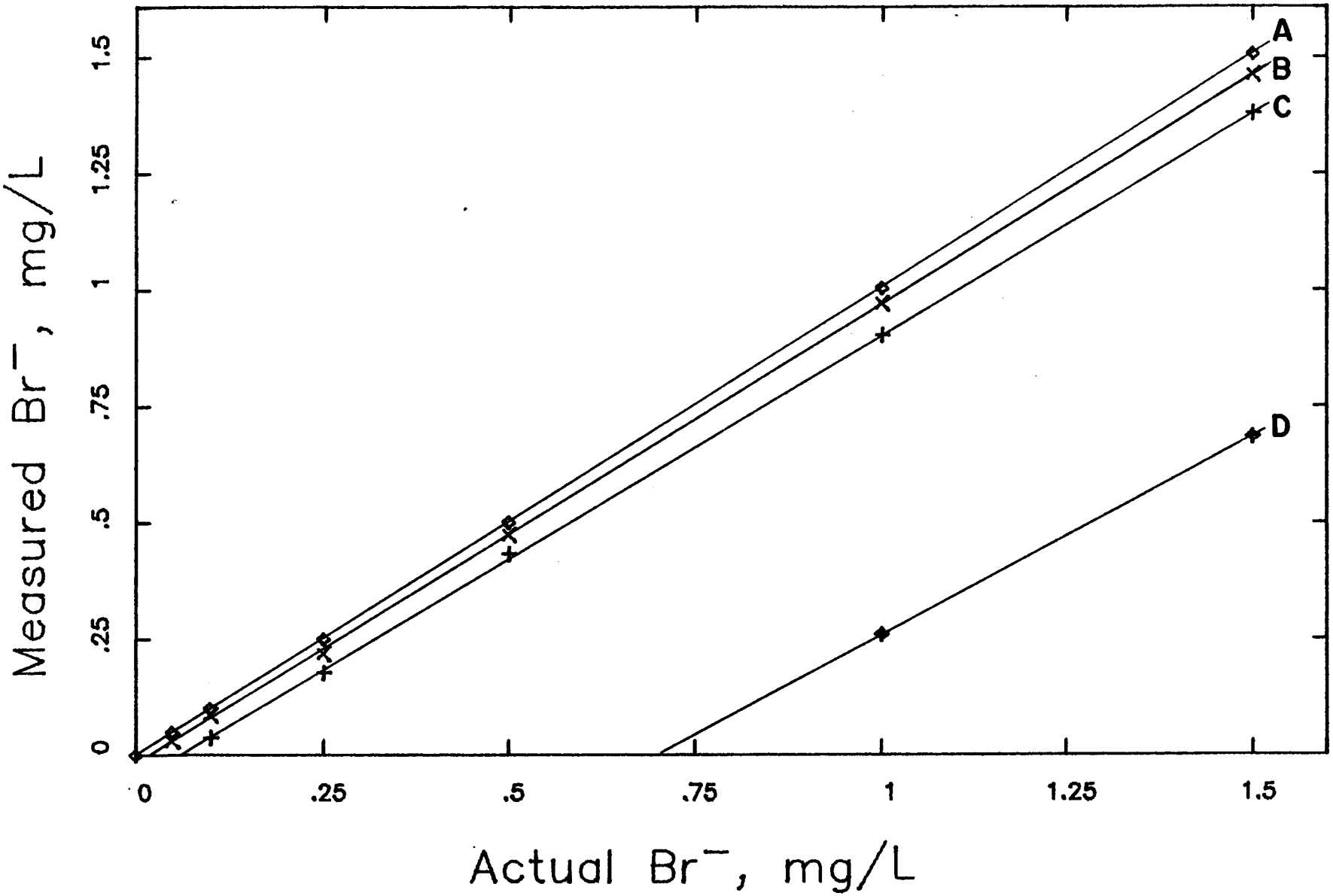
The solution with an ionic strength of 5.5 worked best, but a brown oily substance developed upon addition of the surfactant. Therefore, the next best buffer, which had an ionic strength of 5.1, was used. It contained acetate buffer, sodium nitrate, magnesium sulfate, and Brij-35 surfactant (see Experimental Section). The ionic strength of the reaction mixture due to the ionic strength/pH buffer is 0.27 M. The largest increase in ionic strength in the reaction mixture contributed by a natural water should be approximately 0.5% of this (saline waters and brines are diluted before analysis), and, therefore, represents a negligible change.

The effect of the ionic strength/pH buffer is shown in Table 4. The positive interferences were reduced to insignificant levels except for chloride and bicarbonate, both of which still caused substantial positive interferences.

b. Ammonia interference

A significant interference occurs for ammonia levels as low as 0.05 mg/L. The curves showing the extent of the ammonia interference (Figure 8) were obtained by adding known amounts of ammonia to bromide standards and determining the bromide concentration, without using the ion-exchange column. The ammonia interference is less for the automated method than it is for the manual method. Ion exchange was effective

Figure 8. Effect of Ammonia on Measured Bromide for the Automated Phenol Red Method: (A) 0.0 mg/L NH_3; (B) 0.05 mg/L NH_3; (C) 0.1 mg/L NH_3; (D) 0.5 mg/L NH_3. Each point represents an average of three measurements.


Measured Br⁻, mg/L
0
.25
.5
.75
1
1.25
1.5
Actual Br⁻, mg/L
A
B
C
D

in this study as for the manual method (Table 5). Ammonia removal is essentially complete, and a corresponding increase in measured bromide concentration occurs in all cases.

The bromide determinations were made with and without the ion-exchange column in the automated system. To determine the amount of ammonia which would be present during the determination of bromide, the ammonia determinations were made with and without the ion-exchange column and the pre-pump debubbler from the bromide system. When used, these were placed before the reagent addition section of the automated ammonia system as for the bromide determination (Figure 6).

With the ion-exchange column placed in the ammonia determination system, a calibration curve cannot be obtained. Therefore, ammonia standards for the ammonia determination with ion exchange were run with only the pre-pump debubbler, which is necessary for an accurate measurement for both the standards and the samples or spiked bromide standards because it removes part of the sample stream, thereby lowering the signal. A slight deviation is present in the ammonia calibration curve because the sample spread characteristics, which affect the signal magnitude, are different without the ion-exchange column in the system.

To obtain a practical measure of the capacity of the ion-exchange column and its ability to remove ammonia in the presence of high concentrations of other cations, the following study was done. The bromide concentration in a sample with

Table 5. Effect of Ion Exchange on the Automated Determination of Bromide and Ammonia in Bromide Standards Spiked with 0.5 mg/L Ammonia and in Natural Waters

		Measured concentrations, mg/L[a,b]			
		Without ion exchange		With ion exchange	
Bromide, mg/L in standard		Ammonia	Bromide	Ammonia	Bromide
0.05		0.50	<0.00[c]	0.00	0.05
0.10		0.50	<0.00	0.00	0.10
0.25		0.49	<0.00	0.00	0.25
0.50		0.50	<0.00	0.00	0.50
1.00		0.50	0.26	0.00	1.00
1.50		0.50	0.68	0.00	1.49
Sample[d]	Dilution[e]				
OFB3	1/100	0.15	0.81	0.00	1.08
SOFB2	1/100	0.36	0.36	0.00	0.92
HSB1	1/100	0.04	0.22	0.01	0.24
SHSB2	10/100	0.05	0.14	0.01	0.19[f]
F5	none	0.06	0.10	0.00	0.15

[a]Values represent an average of three measurements.

[b]Bromide values are corrected for the chloride interference.

[c]Signal depressed below baseline.

[d]OFB = oil-field brine; F = fresh groundwater; HSB = halite-solution brine; SOFB = saline water (freshwater polluted with oil-field brine); SHSB = saline water (freshwater contaminated with halite-solution brine).

[e]Dilution of sample prior to determination.

[f]The measured bromide concentration for SHSB2 has not changed from that found for the manual method. This is probably due to loss of carbon dioxide and precipitation of carbonate (positive interferents) between the time of the manual method bromide determination and the automated bromide determination (9 months). Removal of ammonia (negative interference) increased the signal by an equal amount.

high total dissolved solids (approximately 4000 mg/L), 0.46 mg/L ammonia, and 0.6 mg/L bromide was measured 20 consecutive times. No significant change in measured bromide concentration was noted, indicating that recharging the column once an hour is more than sufficient.

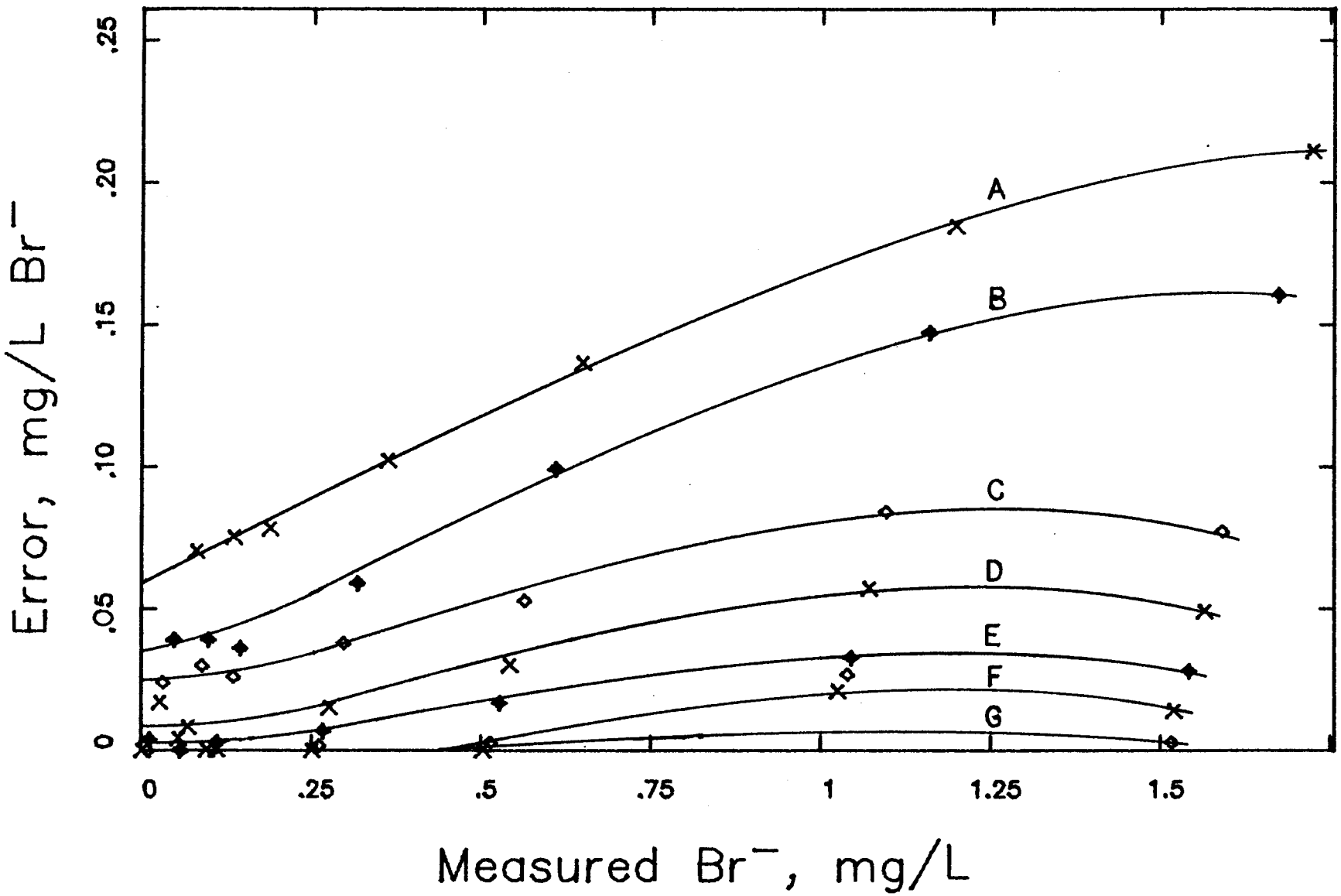
A discussion of the cause of the ammonia interference can be found in the manual method section.

c. Chloride interference

A significant positive interference occurs for chloride levels as low as 100 mg/L. Curves showing the bromide error due to chloride interference (Figure 9) were obtained by adding known amounts of chloride to bromide standards and measuring the bromide concentration, which is the sum of the actual bromide and the apparent bromide due to chloride. The chloride interference is much less for the automated method than it is for the manual method.

As for the manual method, these curves can be used to correct for the chloride interference. The chloride and bromide in the samples are determined in separate measurements. The correction for the chloride concentration present is determined from a curve (or interpolation between curves) at the measured bromide concentration. This correction is then subtracted from the measured bromide concentration to give the actual bromide content. For example (see Figure 9), the chloride correction for a sample with measured bromide and chloride concentrations of 0.60 mg/L and 1000 mg/L,

Figure 9. Error in the Automated Determination of Bromide Caused by Chloride Using the Ionic Strength/pH Buffer: (A) 2000 mg/L Cl; (B) 1000 mg/L Cl; (C) 500 mg/L Cl; (D) 200 mg/L Cl; (E) 100 mg/L Cl; (F) 50 mg/L Cl; (G) 25 mg/L Cl. Each point represents an average of three measurements.


Error, mg/L Br⁻
.25
.20
.15
.10
.05
0
A
B
C
D
E
F
G
0
.25
.5
.75
1
1.25
1.5
Measured Br⁻, mg/L

respectively, would be 0.10 mg/L bromide, giving an actual bromide concentration of 0.50 mg/L (see graphical example in Figure 1 for manual method). The effect of applying the correction is shown in Table 6. The correction works exceptionally well for standards. For natural water samples the correction is good to within a few percent, or better, as indicated by the recovery study.

A much higher chloride interference was seen when the dilute pH buffer was used (Figure 10). This indicates that the chloride interference consists of both an ionic strength component (minimized with the ionic strength/pH buffer) and an effect intrinsic to chloride.

As explained in the manual method section, a plot of chloride concentration versus apparent bromide due to chloride should not be used for this method, and adding a set chloride level to bromide standards will also not work. In addition, because the specific qualitative and quantitative properties of the chloride correction curves depend on the design of the analytical system, they need to be generated for the instrumentation used.

A faster measurement time might minimize the chloride interference because of its slower rate of reaction (13) compared to bromide, but the sensitivity for bromide would also decrease.

Table 6. Effect of Chloride Correction on the Automated Determination of Bromide in 0.50 mg/L Bromide Standards Spiked with Chloride and in Natural Waters

Chloride, mg/L in bromide standards	Measured bromide, mg/L[a,b] Uncorrected	Corrected[c]
50	0.50	0.50
100	0.52	0.50
500	0.55	0.50
1000	0.60	0.50
2000	0.64	0.50

Sample[d]	Dilution[e]	Chloride, mg/L[f]		
OFB3	1/100	285	1.13	1.07
SOFB2	1/100	277	1.00	0.94
HSB1	1/100	1930	0.34	0.23
SHSB2	10/100	948	0.24	0.18[g]
F5	none	25	0.14	0.14

[a]Values represent an average of nine measurements.

[b]Measurements done with ion-exchange column to remove ammonia.

[c]Correction derived from data shown in Figure 9.

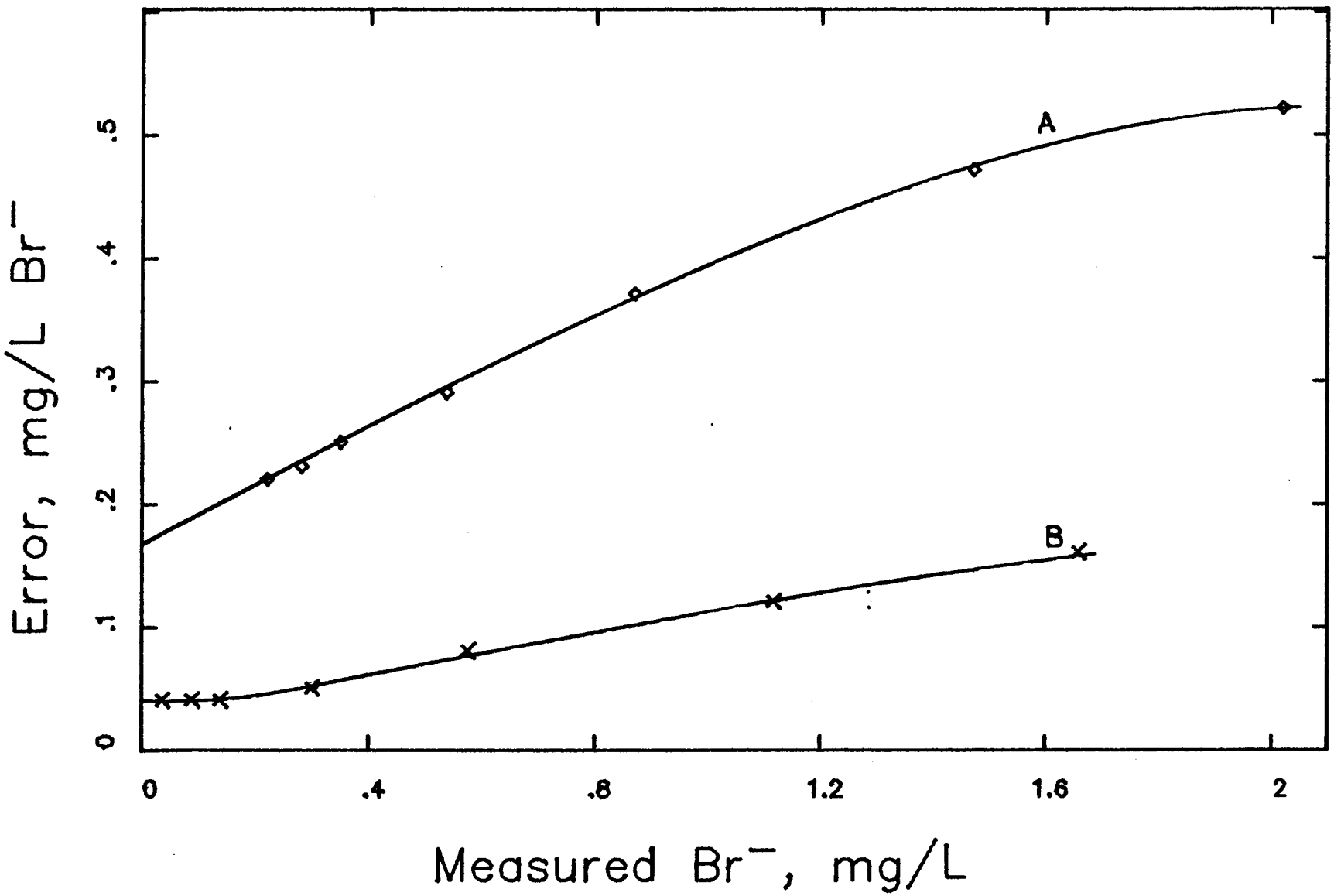
[d]OFB = oil-field brine; F = fresh groundwater; HSB = halite-solution brine; SOFB = saline water (freshwater polluted with oil-field brine); SHSB = saline water (freshwater contaminated with halite-solution brine).

[e]Dilution of sample prior to bromide determination.

[f]Determined separately by method given in reference 22 or by argentometric titration.

[g]See footnote f, Table 5.

Figure 10. Error in the Automated Determination of Bromide Caused by Chloride Using the Dilute pH Buffer: (A) 1000 mg/L Cl; (B) 100 mg/L Cl. Each point represents an average of three measurements.

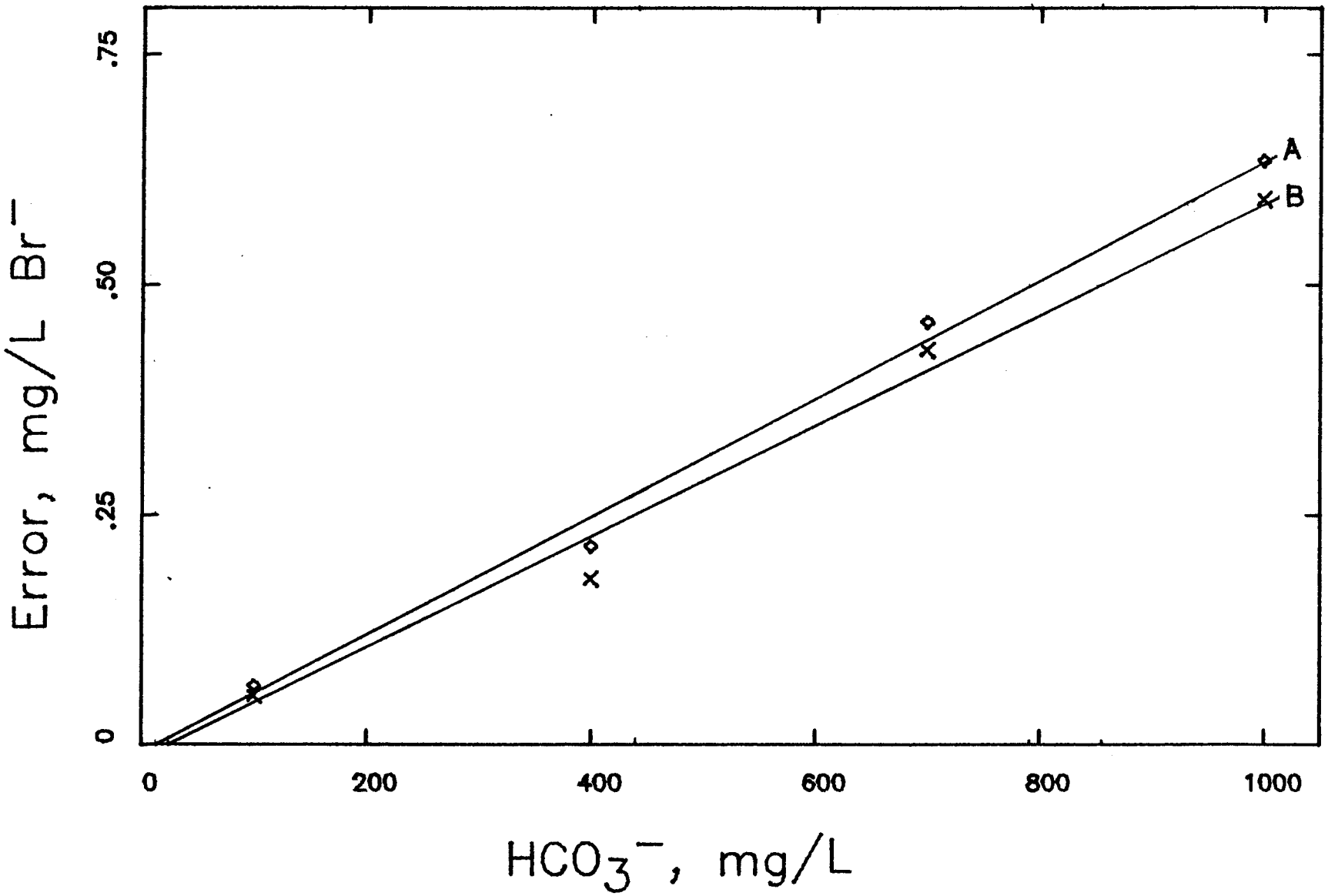

Error, mg/L Br⁻
0
.1
.2
.3
.4
.5
A
B
0
.4
.8
1.2
1.6
2
Measured Br⁻, mg/L

d. Bicarbonate interference

Bicarbonate is a significant interference in the automated bromide method for levels as low as 50 mg/L (Figure 11). The data were obtained by measuring the bromide concentration in sodium bicarbonate standards adjusted to pH 7.3, which is a typical groundwater pH, with and without 0.5 mg/L bromide added. The actual bromide concentration present in the spiked bicarbonate standards was subtracted from the measured value to give the apparent bromide concentration (error) due to bicarbonate. Because there is no actual bromide in the unspiked samples, the measured value for them is the apparent bromide concentration (error) due to bicarbonate. The two curves are approximately collinear, suggesting that this is not an interactive effect as it is for chloride, although further characterization is needed to be certain. The reason the errors seen at 400 mg/L bicarbonate are below the curves may be due to a dilution error.

An average of the two curves in Figure 11 can be used as a correction curve. The bicarbonate and bromide concentrations are determined in separate measurements. The bromide correction for the bicarbonate concentration present is determined from the curve. This value is then subtracted from the measured bromide to give the actual bromide. For example (see Figure 11), the bicarbonate correction for a sample with measured bromide and bicarbonate concentrations of 1.0 mg/L and 500 mg/L, respectively would be 0.34 mg/L bromide, giving

Figure 11. Error in the Automated Determination of Bromide Caused by Bicarbonate: (A) No bromide added to bicarbonate standards; (B) 0.5 mg/L bromide added to bicarbonate standards, with 0.5 mg/L bromide subtracted from measured bromide to give apparent bromide. Each point represents an average of three measurements.


Error, mg/L Br⁻
.75
.50
.25
0
A
B
0
200
400
600
800
1000
HCO3⁻, mg/L

an actual bromide concentration of 0.66 mg/L.

That this interference is due to a pH change caused by the bicarbonate was suggested by the much greater bicarbonate interference which occurred with the use of the dilute pH buffer than with the ionic strength/pH buffer (Table 4). Even the greater capacity of the ionic strength/pH buffer is not sufficient to buffer against small pH changes for samples with high bicarbonate levels. This interference has been noted by others (11). Acidification of bicarbonate standards spiked with bromide to a pH of approximately 4.6 with dilute nitric acid prior to bromide determination reduced the bicarbonate interference to an insignificant level.

Titration of BPB, which is probably the major reaction product, over the pH range of 3.9 to 7.7, showed that the reaction pH of 4.6 is within the transition interval for the acid and basic forms of BPB, where a small increase in pH causes a large increase in absorbance at 590 nm. Although a complete titration curve was not obtained, the results seem to agree well with the literature equivalence point of 3.95.

Manually combining the final automated method reagents, including the ionic strength/pH buffer, with water or 1000 mg/L bicarbonate in the same volume proportions as in the automated method, showed that the pH is indeed increased significantly (0.1 pH units) by the presence of bicarbonate. The pH did not change with time during 15 minutes of the phenol red reaction, indicating that the bicarbonate inter-

ference does not change with time.

As with chloride, addition of bicarbonate to the bromide standards is not a suitable compensation technique because, unlike seawater (13), bicarbonate is quite variable in the samples studied.

For solutions with high bicarbonate concentrations, it may be advisable to use a buffer of pH 6.0 where the absorbance of bromophenol blue is insensitive to changes in pH. However, the overall consequences, such as the effect on other interferences, have not been evaluated fully. Also, the reaction may proceed at a much slower rate at a higher pH (32).

C. Reaction Product Characterization and the Cause of the Chloride Interference

A study of the chemistry of the phenol red method was undertaken when it was noted that the color produced by the reaction with bromide standards was visually the same as that for chloride standards and for the distilled, deionized water blank.

To determine whether the reaction product was actually BPB, spectra of BPB and PR in the manual method buffer were acquired. Using the manual method procedure, spectra of reaction products for bromide, chloride, and combination bromide-chloride standards, for various samples, and for water were also recorded and compared to those of BPB and PR. The major wavelengths of maximum absorbance are listed in Table 7 (see Figure 5 for spectra shape). The values suggest either that the absorbance maximum of BPB is shifted slightly toward a shorter wavelength due to solvent or solute effects or, more likely, that the reaction product is not exclusively BPB. In each case, the magnitude of the longer wavelength maxima increased and that of the shorter wavelength maxima decreased as the reaction proceeded. This is expected for a decrease in the PR concentration (shorter wavelength maxima) due to halogenation to form the reaction product (longer wavelength maxima).

If the reaction product is not exclusively BPB, other products may be partially or totally chlorinated compounds,

Table 7. Wavelengths of Maximum Absorbance for Solutions of Bromophenol Blue (BPB), Phenol Red (PR), and Products of the Reaction of Standards, Distilled/Deionized water, and Natural Water Samples. Instrument settings are given in Appendix A.

	Wavelengths, nm[a]	
Solution	λ1	λ2
BPB[b]	590	384
PR[b]	-	429
0.5 mg/L bromide	588	440
0.5 mg/L bromide + 800 mg/L chloride	588	440
800 mg/L chloride	588	440
distilled/ deionized water	588	438
natural water samples	588	436

[a]Values to within ± 0.5 nm, except that for the natural water samples, which is an average of 5 different samples with a standard deviation of ± 1.2.

[b]In pH 4.6 buffer prepared as described in reference 8.

such as 3,3'-dichlorophenolsulfonephthalein (chlorophenol red), 3,3'-dibromo-5,5'-dichlorophenolsulfonephthalein (bromochlorophenol blue), or 3,3',5,5'-tetrachlorophenolsulfonephthalein (chlorophenol blue) or a partially brominated compound such as 3,3'-dibromophenolsulfonephthalein (bromophenol red) (12,33,34). Chlorophenol red absorbs near 575 nm, but when used in place of PR, the wavelength of the maximum absorbance increases as the reaction proceeds. This is probably due to further halogenation. Bromochlorophenol blue and chlorophenol blue are reported to absorb in the same wavelength region as BPB in this pH range (12,33,34).

Phenol red derivatives with additional halogenation on the sulfonated phenyl ring have been reported (33). Some of these derivatives would absorb in the same region as BPB, but their formation in the phenol red reaction is unlikely because this ring would be least susceptible to electrophilic substitution due to the presence of the deactivating sulfonate group.

The blue color produced by the blank may be explained as follows. When chloramine-T dissociates in an aqueous solution at pH 4.6, predominantly hypochlorous acid is formed (35):

$$H_3C{\cdot}C_6H_4{\cdot}SO_2NHCl + H_2O \rightleftharpoons H_3C{\cdot}C_6H_4{\cdot}SO_2NH_2 + HOCl$$

Hypochlorous acid, or other chlorine-containing substances in equilibrium with it and capable of electrophilic aromatic substitution, may chlorinate PR. Indeed, the reaction product

formed when 5% chlorine water was used instead of chloramine-T with a blank solution prepared manually (but with the same reagents and proportional volumes as used in the automated method) was a similar color to that seen with chloramine-T and absorbed at 590 nm, contrary to an earlier report (26). Chlorination would be expected to occur at the positions ortho to the hydroxy groups of PR as bromination does. Species responsible for this chlorination may be HOCl, H_2OCl^+ and/or Cl_2 (36,37).

The chloride interference may be explained by the reaction of $HOCl/H_2OCl^+$ with chloride to produce chlorine, a stronger chlorinating agent than $HOCl/H_2OCl^+$:

$$HOCl + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O$$

An alternative mode of chloride interference must be considered if chloramine-T disproportionates to form dichloramine-T (38,39) at this pH. If this is the case, then chlorination of phenol red by dichloramine-T is probably the cause of the absorbing blank.

A different oxidizing agent for bromide that would not itself lead to chlorination of PR or oxidation of chloride should eliminate the absorbing blank and the chloride interference.

D. Application of the Improved Phenol Red Method to the Differentiation of Saltwater Pollution Sources in Natural Waters

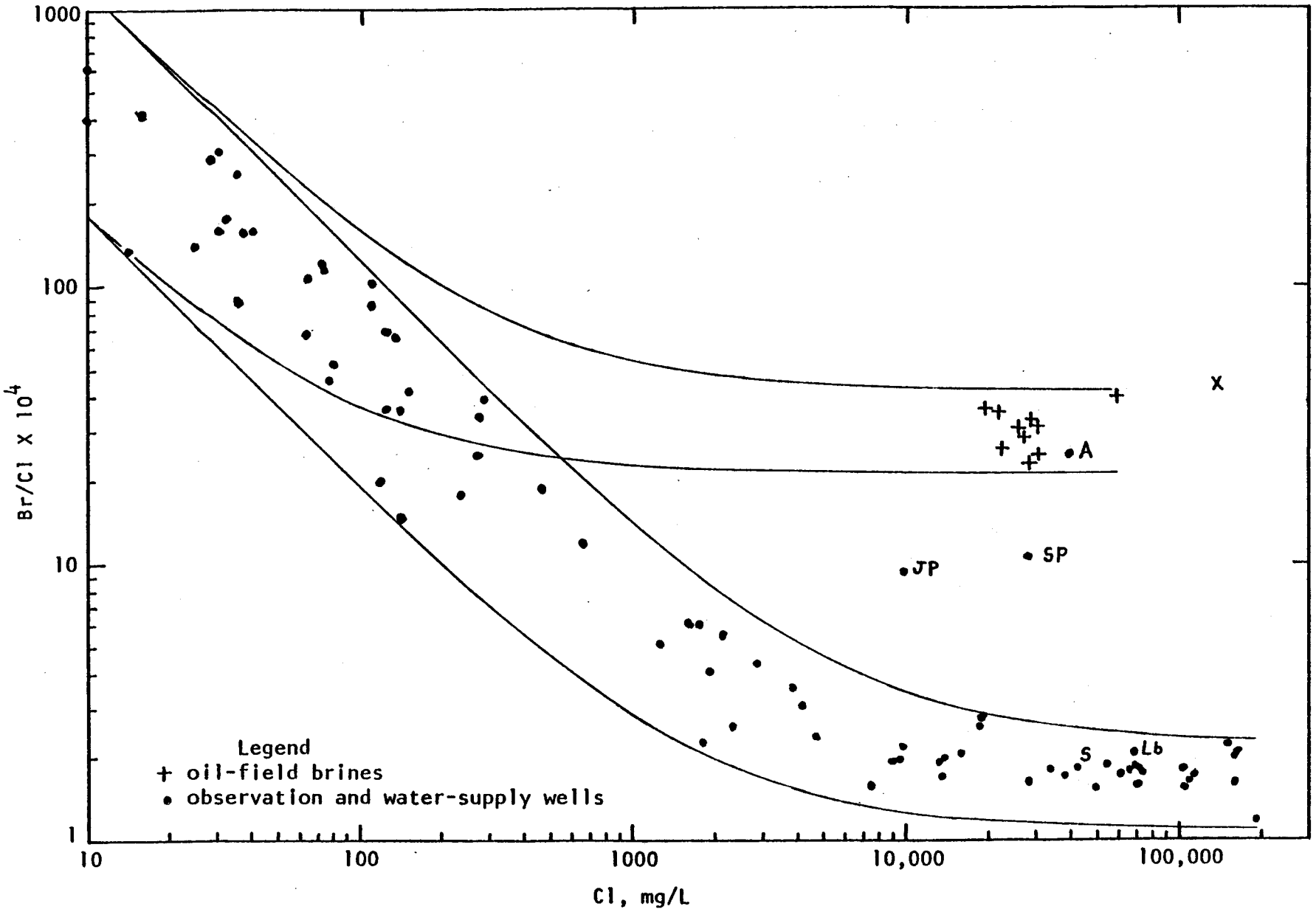
The concentration ratio of bromide to chloride is indicative of the source of saltwater contamination of natural waters (3,4). At a given chloride concentration, this ratio is larger for oil-field brines or waters polluted by oil-field brines than it is for halite-solution brines or waters contaminated by halite-solution brines. The improvements in the phenol red method have made this differentiation more accurate.

Maximum concentrations of ammonia, bicarbonate, and chloride in freshwaters (less than 1000 mg/L total dissolved solids) are generally less than 0.1 ml/L, 500 mg/L, and 400 mg/L, respectively. Samples near the value given for bicarbonate will exclude the possibility of having a chloride concentration this high, and vice versa. For a typical sample of freshwater containing 0.25 mg/L bromide, these values represent errors of approximately -20%, +120%, and +15%, respectively, as found for the automated method without interferent compensations (see Results and Discussion). Maximum concentrations of ammonia and bicarbonate for a halite-solution brine are roughly 5 mg/L and 2000 mg/L, respectively. A typical halite-solution brine saturated with respect to halite (190,000 mg/L chloride) contains a bromide concentration of 40 mg/L. In a sample diluted to 2000 mg/L chloride

to reduce the chloride interference, these values represent errors of approximately -10% and +5%, respectively, while the chloride error is +50%, for a total error of approximately +45%. A typical oil-field brine will contain from 50 to 250 mg/L bromide with a bromide-to-chloride weight ratio of 0.002 to 0.005. Maximum concentrations of ammonia and bicarbonate are approximately 2000 mg/L each. A typical oil-field brine containing 100 mg/L bromide, 30,000 mg/L chloride, 20 mg/L ammonia and 500 mg/L bicarbonate would be diluted 1/100 to bring the bromide concentration within the range of the method. The diluted chloride, ammonia, and bicarbonate concentrations would then represent errors of approximately +6%, -35%, and 0%, respectively, for a total error of -30%. All of these values may, in some cases, vary greatly from those given. For mixtures of any of these three water types, these values will change depending upon the relative proportion of each type within the mixture.

The effect that eliminating these errors has on the ability to differentiate the source of saline pollution in waters can be seen by comparison to the uncorrected values in Figure 12, which is taken from another study (4). This curve was obtained by determining the bromide and chloride concentration in several groundwaters, and plotting the bromide-to-chloride concentration ratio found x 10^4 versus the chloride concentration. The bromide determinations were made using the manual phenol red method (8), using a chloride

Figure 12. Variation in the Weight Ratio Bromide/ Chloride with Chloride Concentration. Labeled points refer to water samples with name abbreviations in Results and Discussion, Section D. Curves are the boundaries of mixing zones of fresh-waters with oil-field brines and salt-solution brines. (Reproduced from Reference 4.)


1000
100
10
1
Br/Cl X 10^4
10
100
1000
10,000
100,000
Cl, mg/L
Legend
+ oil-field brines
• observation and water-supply wells
A
JP
SP
S
Lb
X

correction similar to that given in this study. The ammonia and bicarbonate interferences were not eliminated. Chloride was determined as discussed in the Experimental Section.

Redetermination of the bromide concentration in the samples labeled SP and JP using the improved automated phenol red method increased the bromide-to-chloride x 10^4 concentration ratios to 33.8 and 43.6 from 10.4 and 9.2, respectively. These values are well within the boundaries for the oil-field brines shown in this figure. The bromide concentration in the samples labeled A, S, and Lb were also redetermined using the automated phenol red method. The ratios for these samples did not change significantly. Sample A had a lower ammonia concentration than SP and JP, and therefore would not be expected to change as much upon redetermination. Samples S and Lb, which are halite-solution brines, would not be expected to change much because the chloride interference has already been compensated for in the samples in Figure 12. Only changes due to compensation for bicarbonate and ammonia would be appreciable upon redetermining the bromide concentration in the samples with the automated phenol red method.

Considering only the possible ammonia and bicarbonate errors that may be present before redetermination, freshwaters, halite-solution brines, and oil-field brines may exhibit total errors of +100%, -5%, and -35%, respectively. The effect on Figure 12 of removing these errors would be to raise the halite-solution zone approximately 5%, raise the

oil-field-brine zone approximately 35%, and lower the fresh water zone approximately 100%. Greater differentiation between waters with high chloride concentrations could then be obtained. Greater differentiation between freshwaters containing small amounts of oil-field brines or halite-solution brines would probably be obtained also, because the samples of waters polluted by oil-field brine would probably have had a higher ammonia concentration, and would be lowered less than for other water samples.

The increase in precision may help to differentiate the water types with chloride concentrations below 1000 mg/L which, as shown in Figure 12, are not well separated with the bromide-to-chloride x 10^4 versus chloride curve. By removing analytical scatter amongst these samples, only scatter due to different water types will remain, hopefully giving a better separation.

VI. CONCLUSIONS

A. Comparison of Improved Phenol Red Method with the Standard Phenol Red Method

Automation and interferent compensation for the phenol red method for bromide determination have provided several advantages over the standard manual method (8). The automated phenol red method has a greater sample throughput (20 samples per hour), a lower detection limit (0.01 mg/L), and is less tedious and time-consuming than the standard method. Automation has also increased the precision and accuracy of the method.

The accuracy of the method has improved greatly due to the minimization of the ammonia, chloride, and bicarbonate interferences. The ionic strength interference is insignificant in the standard manual method. The compensation procedures for chloride and ammonia work well for both the automated and manual methods, and undoubtedly the bicarbonate interference compensation procedures will work well for the manual method as well as the automated method. The chloride and ammonia interferences are both less for the automated method than for the manual method.

The precision of the automated phenol red method (approximately 3.5 % RSD at 0.25 mg/L bromide, see Appendix B) is also better than that of the manual method. A rough precision determination for the manual method was made by measuring the

bromide concentration in a sample three times. A chloride correction was applied. No correction procedure was used for ammonia. The average concentration found was 0.27 mg/L bromide, with a % RSD of 19. This increase in precision is undoubtedly due to automation, which lowers the chance for human error.

B. Comparison of Improved Phenol Red Method with Other Common Standard Methods

Three very common publications exist which compile standard methods for the analysis of water. These are published by the U.S. Environmental Protection Agency (EPA), the U.S. Geological Survey (USGS), and the American Public Health Association (APHA).

A comparison of the standard phenol red method (8), which is recommended by the APHA, with the improved automated phenol red method can be found in the preceding chapter.

The USGS recommends two methods for the determination of bromide in water (40,41). One method is for low ranges, while the other is for high ranges of bromide concentrations.

The method for low bromide concentrations (40) is based on the ability of bromide to catalyze the oxidation of iodine to iodate by permanganate in acid solution. The temperature must be kept at or near 0° C. After a given time, the excess iodine in the solution is extracted with carbon tetrachloride and the bromide concentration is determined indirectly by measuring the absorbance of the extract. This method has been

automated (5,6) and is being used by the USGS laboratories in Denver.

In the manual catalytic-oxidation method, the timing and reaction temperature must be controlled by the analyst. All reagent additions and mixing must also be performed by the analyst. The improved phenol red method is easier to use because all processes essential to the reaction are automatically controlled. This also reduces the chances for error. The result is better precision, 1 to 8% RSD for the improved phenol red method, depending on concentration, as opposed to 2 to 30% RSD for the catalytic-oxidation method. The analyst risks exposure to carbon tetrachloride and must clean more glassware when using the catalytic-oxidation method. Because the automated phenol red system is completely enclosed and requires no reaction vessels, the analyst does not need to clean as much glassware.

Several interferences, including silver, iodide, zine, manganese, and iron are mentioned for the catalytic-oxidation method. These are probably all negligible interferences in most natural waters. Chloride was found to be a major interferent for the automated catalytic-oxidation method (6,7), making this method unacceptable for the saline samples of interest in this study. A correction curve was used to correct for this interference (6), but the interference was still found to be unacceptable for halite-solution brines (4). Chloride probably also interferes in the manual catalytic-oxidation method. The automated phenol red method appears

to suffer from more interferences, but they are easily minimized.

The detection limit for both methods is 0.01 mg/L. The applicable concentration range of the automated phenol red method is larger than that for the catalytic-oxidation method; 0.01-1.5 mg/L as opposed to 0.01 to 0.1 mg/L. For bromide concentrations between 0.1 mg/L and 1.0 mg/L, the USGS recommends dilution and use of the catalytic-oxidation method. For samples containing more than 1.0 mg/L bromide, the USGS recommends use of the hypochlorite-oxidation titrimetric method (41).

The hypochlorite-oxidation method is based on the oxidation with hypochlorite of iodide and bromide to iodate and bromate, respectively. The iodate and bromate are converted to equivalent amounts of iodine by the addition of iodide and acid. The iodine is titrated iodometrically, and the iodine concentration is related to the sum of the bromide and iodide concentrations in the initial sample. The iodine concentration in the initial sample is determined using the same procedure with bromine water instead of hypochlorite. The iodine concentration is then subtracted from the bromide and iodide to give the bromide concentration. This is one major disadvantage of this method--the need to make two determinations per sample.

Due to automation, the improved phenol red method is much faster and less tedious than the hypochlorite-oxidation titrimetric method, as discussed for the catalytic-oxidation

method. The hypochlorite-oxidation titration method suffers interference from iron, manganese, and organic materials. These interferents are precipitated out with calcium oxide in a tedious manual procedure. The interferences to the improved phenol red method are easily compensated.

The improved automated phenol red method is slightly more precise than the hypochlorite-oxidation titrimetric method. At 0.25 mg/L bromide the automated phenol red method has a % RSD of approximately 3.5, and the hypochlorite-oxidation titrimetric method has a % RSD of approximately 4.4.

The improved phenol red method has a much lower detection limit than the hypochlorite-oxidation titrimetric method, which has a detection limit of 1.0 mg/L. However, samples with much higher bromide concentrations can be analyzed without dilution using the hypochlorite-oxidation titration method--up to roughly 20 mg/L--as discussed below.

The EPA also recommends the hypochlorite-oxidation titration method for the determination of bromide (42). The EPA gives an applicable bromide concentration range of 2 to 20 mg/L, with precision of roughly 2 to 13% RSD over this range. The improved phenol red method is more precise and applicable to lower bromide concentrations. Recovery studies for the hypochlorite-oxidation method produced an average recovery of 93.8 ± 7.8%, with a range of 83 to 99%. The improved phenol red method, which has an accuracy of 98.4 ± 4.9%, with a range of 91.2 to 106%, is more accurate.

In summary, the improved phenol red method provides a

faster, more precise method than either of the two standard methods discussed above, with a detection limit as low or lower.

C. Recommended Future Research

The use of flow injection analysis (FIA) to automate the phenol red method may have several advantages, such as controllable sample dispersion, higher sample throughput, and smaller sample size (21,43,44). Preliminary work to automate the phenol red method using FIA was done in this study. The detector used was a GCA/McPherson 700 series UV-VIS spectrophotometer with a stopped-flow kinetics flowcell. The pump used was a Laboratory Data Control dual minipump. All tubing used was 0.8 mm i.d. teflon. The reagents were prepared by dilution of the SFA reagents, including the dilute pH buffer in order to make the reagent concentrations in the flow stream similar to those in the reaction mixture of the manual method (8) reaction mixture. This was done by mixing 4 mL of the phenol red and buffer solutions together and diluting to 100 mL. Also, 4 mL of the chloramine-T reagent was diluted 4/100. The reagents were pumped together at a rate of approximately 0.2 mL/min and the sample was injected into the reagent stream with an HPLC injection loop. The stream then flowed through a coil of tubing which delayed the measurement of absorbance at 590 nm by approximately 2.5 minutes.

It appears that one major problem of the system is that upon addition of the sample slug into the reagent stream, the colored reagent stream is diluted, decreasing the absorbance.

Positive peaks have been obtained only for highly concentrated bromide standards (1.5 and 5 mg/L), because they react to form a large enough concentration of the colored product to offset the dilution of the blank absorbance. Heating the delay coil may eliminate this problem. Linearity has not yet been established.

Use of the initial rate kinetic method of analysis may eliminate some of the interferences, but may not be worth the effort. The slope (rate) of the absorbance-versus-time curve should be proportional to the initial bromide concentration in the early stages of the reaction. Interferences which react in a similar way as bromide and which have rate constants much smaller than that of bromide should only affect the actual absorbance and not the change in absorbance; therefore, their interference would not be seen. This may work for the chloride interference, because its mode of interaction is similar to that of bromide, but its rate constant is probably much lower. The ammonia interference might be eliminated with this method if it reacts with the oxidant in the reaction or with bromine at a slow rate. The ionic strength interference would probably not be eliminated because it alters the rate of the analyte reaction. It is unknown at this time whether the change in pH caused by bicarbonate has any effect on the reaction rate--if it does, then this method would not eliminate the bicarbonate interference.

The initial rate method may expand the analytical range to higher bromide concentrations, because higher bromide

concentrations increase the reaction rate. This may eliminate the problem in the present method with highly concentrated samples fading before being measured.

Another negative interferent has been discovered in a few water samples. This may be nitrite. This interferent should be identified, characterized, and minimized.

It might be possible to find experimental conditions under which the chloride interference is independent of the bromide concentration. This would greatly simplify the correction procedure. If the bromide dependence of this interference is due to the competition between bromide and chloride for phenol red, an increase in phenol red concentration might reduce this dependence to an insignificant level. A plot of apparent bromide versus chloride could then be used as a correction curve.

Further work with the characterization and elimination of the bicarbonate interference should be done. As suggested in the Results and Discussion Section, use of a higher pH buffer may eliminate this interference, although some unforseen negative consequences might occur as well.

Also, as suggested earlier, a different oxidant for bromide might be found which would not lead to chlorination of phenol red or oxidation of chloride, thereby eliminating the absorbing blank and the chloride interference.

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Appendix A

Perkin-Elmer 555 Instrument Settings for Spectral Studies

ABS (absorbance): scale high = 1.0 scale low = 0.0

Slit (bandpass): 1 nm

Response Time: 0.5 s

Speed (scan): 120 nm/min

Recorder, nm/cm: 4

Cycle Time: 6 min

Wavelength Range: 800 to 350 nm

Rep Scan (repetitive scan, not used for scan of BPB and PR indicator solutions)

Cont (continuous, not used for scan of BPB and PR indicator solutions)

Over (overlayed presentation of spectra, not used for scan of BPB and PR indicator solutions)

Full range background correction performed before obtaining results

Cells: Glass

Reference Solution: Water plus buffer (standard method proportions and buffer concentration (8)).

Appendix B

Automated Method Precision Data

Nine measurements for each sample were obtained over a four-day period. Sample description data can be found in Appendix D.

Sample location[a]	Measured bromide, mg/L[b]									Average bromide mg/L	% RSD
13-1E-230AB	0.178	0.168	0.093	0.129	0.115	0.138	0.142	0.160	0.160	0.142	19.1
17-3W-8CCB	0.160	0.181	0.148	0.138	0.162	0.156	0.166	0.181	0.158	0.161	8.66
15-3W-19AAA	0.180	0.195	0.166	0.170	0.179	0.185	0.160	0.179	0.202	0.180	7.45
13-1W-16DCC2	0.183	0.182	0.196	0.191	0.156	0.189	0.170	0.182	0.185	0.181	6.48
13-1W-10DCA	0.210	0.200	1.173	0.175	0.186	0.197	0.242[c]	0.117[c]	0.199	0.191	7.22
14-1W-3BBC	0.206	0.195	0.187	0.198	0.192	0.202	0.201	0.219	0.203	0.200	4.58
14-1W-7AAD	0.257	0.238	0.254	0.218	0.151	0.235	0.189	0.209	0.215	0.218	15.3
13-1E-20ACA	0.233	0.230	0.204	0.253	0.190	0.211	0.241	0.208	0.249	0.224	9.78
24-13W-31DDC	0.220	0.246	0.217	0.227	0.230	0.247	0.233	0.233	0.227	0.231	4.43
13-3W-33BCC	0.229	0.243	0.238	0.231	0.231	0.242	0.217	0.238	0.266[c]	0.234	3.65
13-2W-24ACC	0.288	0.287	0.238	0.279	0.233	0.248	0.270	0.269	0.283	0.266	7.98
15-3W-7BAA	0.259	0.272	0.252	0.267	0.270	0.269	0.261	0.286	0.262	0.266	3.63
13-3W-16DCD	0.268	0.268	0.270	0.265	0.205[c]	0.250[c]	0.261	0.272	0.270	0.268	1.38
13-2W-32CCB	0.350	0.355	0.356	0.219[c]	0.340	0.347	0.348	0.361	0.355	0.352	1.87
13-1W-30BCC	0.390	0.395	0.367	0.355	0.333	0.340	0.350	0.362	0.381	0.364	5.96
13-2W-33DDC	0.350	0.345	0.414	0.383	0.383	0.333	0.365	0.349	0.327	0.366	6.83

Sample location[a]	Measured bromide, mg/L[b]									Average bromide mg/L	% RSD
16-3W-3CDC	0.485	0.487	0.475	0.493	0.503	0.496	0.489	0.508	0.499	0.493	2.04
13-1W-23CAA	0.468	0.528	0.510	0.504	0.508	0.533	0.497	0.532	0.535	0.513	4.29
13-1W-16DCC	0.562	0.530	0.589	0.611	0.582	0.550	0.551	0.576	0.559	0.568	4.28
13-2W-35DBB	0.588	0.599	0.592	0.635	0.572	0.563	0.595	0.592	0.628	0.596	3.90
25-13W-6ACC	0.706	0.713	0.708	0.713	0.709	0.733	0.723	0.709	0.705	0.713	1.28
14-2W-28ADB	0.816	0.834	0.853	0.914[c]	0.846	0.833	0.833	0.850	0.856	0.840	1.60
14-1W-8BBA	0.865	0.860	0.835	0.849	0.851	0.859	0.828	0.868	0.884	0.885	2.00
14-2W-18BDA	0.915	0.945	0.916	0.920	0.942	0.960	0.920	0.972	0.940	0.937	2.19
14-2W-7D	1.012	1.003	1.034	1.017	.046	1.000	0.999	1.018	1.005	1.015	1.585
14-2W-9CAA	1.077	0.066	1.086	1.052	1.094	1.053	1.053	1.077	1.077	1.071	1.437

[a] Township-range-section, quarter section, quarter-quarter section, quarter-quarter-quarter section (Kansas waters).

[b] Diluted value, see Appendix D.

[c] Value rejected using Q test, not used in average or % RSD calculation.

Appendix C

Automated Method Accuracy Data (recovery study)

Three measurements were taken. Values shown represent average. Sample description data can be found in Appendix D.

Sample location[a]	Bromide, mg/L, measured[b] in unspiked sample	mg/L bromide spike (A)	Δ bromide,[c] mg/L (B)	% Recovery[d]
14-2W-9CAA	1.053	0.250	0.228	91.2
14-2W-28ADB	0.853	0.250	0.233	93.2
14-1W-7AAD	0.224	0.250	0.237	94.8
13-1W-16DCC2	0.189	0.250	0.241	96.4
14-2W-18BDA	0.941	0.250	0.245	98.0
15-3W-7BAA	0.267	0.250	0.258	103
16-3W-3CDC	0.507	0.125	0.120	96.0
13-1E-23DAB	0.153	0.250	0.264	106
13-1W-23CAA	0.522	0.250	0.256	102
13-3W-33BCC	0.245	0.250	0.257	103

[a] Township-range-section, quarter section, quarter-quarter section, quarter-quarter-quarter section (Kansas waters).

[b] Diluted values, see Appendix D.

[c] Bromide, mg/L, measured in spiked sample minus bromide, mg/L, in unspiked sample.

[d] [(A-B)/A] x 100.

Appendix D

Sample Description Data

Wells were sampled in 1981.

Sample location[a]	Water type[b]	Chloride, mg/L[c]	Ammonia, mg/L[d]	Dilution during bromide determination
14-2W-7DB	OFB	59,500	30.5	1/250
14-2W-9CAA	OFB	28,500	15.3	1/100
14-2W-28ADB	OFB	22,000	12.3	1/100
13-2W-33DDC	F	79	0.223	none
13-2W-35DBB	F	1,800	0.459	none
14-1W-7AAD	F	63	0.082	none
13-1E-20ACA	F	10	0.038	none
13-1W-16DCC	F	1,240	0.143	none
13-1W-16DCC2	SHSB	9,480	0.520	10/100
13-2W-32CCB	HSB	160,000	5.70	10/100
14-1W-3BCC	SHSB	3,800	0.188	25/100
13-1W-10DCA	F	35	0.505	none
13-2W-35ACC	F	66	0.403	none
13-3W-16DCD	F	31	0.911	none
14-2W-18DBA	SOFB	27,700	36.3	1/100
15-3W-7BAA	HSB	160,000	6.00	1/100
16-3W-3CDC	SOFB	39,800	11.6	1/200
17-3W-8CCB	SHSB	68,800	4.10	1/100
13-1E-23DAB	F	25	0.058	none

Sample location[a]	Water type[b]	Chloride,[c] mg/L	Ammonia,[d] mg/L	Dilution during bromide determination
13-1W-23CAA	SHSB	19,100	0.430	10/100
13-1W-30BCC	F	235	0.239	none
13-3W-33BCC	HSB	193,000	4.50	1/100
14-1W-8BBA	SHSB	9,800	24.9	1/50
15-3W-19AAA	SHSB	42,400	2.05	1/50
24-13W-31DDC	SOFB	74	0.470	10/100
25-13W-6AAC	OFB	19,100	17.2	1/100

[a]Township-range-section, quarter section, quarter-quarter section, quarter-quarter-quarter section (Kansas waters).

[b]F = fresh groundwater; OFB = oil-field brine; HSB = halite solution brine; SOFB = saline water (F polluted with OFB); SHSB = saline water (F contaminated with HSB).

[c]Chloride concentration in undiluted sample.

[d]Ammonia concentration in undiluted sample (diluted value removed with ion exchange).