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DETERMINATION OF FREE BROMINE IN WATER (u)

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by

T. E. Larson and F. W. Sollo, Jr.

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University of Illinois
Urbana, Illinois 61801

I. SUMMARY

The major objective of this work has been the development of suitable methods for the determination of free bromine and bromamines in water, with emphasis on methods that would be suitable for field use. A number of reagents were screened on the basis of their reaction with H0C1, HOBr, NH_2C1, and NH_2Br. Six reagents -- methyl orange pH 2, DPD oxalate, phenol red, brom cresol purple, phenosafranin, and methyl orange pH 9.5 -- were selected for detailed investigation.

These six methods have been examined for response to mono-, di-, and tribromamine. Test procedures for DPD, brom cresol purple, and phenosafranin have been changed slightly. To promote the complete reaction of bromamines with DPD oxalate, potassium iodide is added to the sample prior to testing. To keep bromamine interference at a minimum for the brom cresol purple and phenosafranin tests, the premixed sample and buffer are added to the reagent.

The methyl orange pH 2, DPD, phenol red, and brom cresol purple tests were used to study the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide ion. The reaction to form bromamines depends primarily upon pH.

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IV. DETERMINATION OF FREE BROMINE IN WATER

A. Introduction

Reportedly bromamines are far more effective disinfectants than the chloramines and approach free bromine in disinfecting power. This property of the bromamines could eliminate the need to reach breakpoint for disinfection of many waters. The major objective of this study has been the development of suitable colorimetric methods for the determination of free bromine and bromamines in water. The possibility for use of chlorine and bromide ion to produce bromine necessitated examination of methods suitable for distinguishing between the halogens. As previously reported, twenty-seven reagents were evaluated for possible use as colorimetric tests for free bromine.

Five reagents were selected for detailed investigation, primarily because interferences due to chloramine, ferric ion, nitrite ion, and manganese are low. The five reagents and the bromine and chlorine species each can determine are:

1. methyl orange, pH 2 -- total bromine and free chlorine,
2. DPD oxalate -- total halogen,
3. phenol red -- total bromine,
4. brom cresol purple -- free bromine,
5. phenosafranin -- free bromine.

Recently, a pH 9.5 methyl orange test has been considered for the determination of free bromine. Although none of these reagents is completely free of interferences, each serves a particular purpose and a combination of the tests may be used to determine both the quantity and form of the total residual halogen present.

The phenosafranin test pH has been raised from pH 9.2 to pH 9.5. Therefore, one buffer may be used for the three free bromine tests.

The six methods have been examined for response to mono-, di-, and tribromamine solutions. The apparent incomplete response of DPD oxalate to tribromamine necessitated a change in test procedure. To promote the complete reaction of tri-bromamine, the sample is mixed with potassium iodide before testing. For the brom cresol purple and the phenosafranin tests, bromamine interference is kept at a minimum by changing the order of addition of reagents.

The methyl orange pH 2, DPD oxalate, phenol red, and brom cresol purple tests were used to study the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide ion. The effect of initial conditions such as pH, ammonium and bromide ion concentrations have been examined in order to determine their relation to the proportion of chloramine and bromamines formed.

The recommended reagents, test methods, and possible application of test methods are discussed individually in the following section. In all figures the data are indicated in terms of the total halogen employed, except where both halogens were present in which case the results are as apparent free bromine.

B. Test Methods

All solutions were prepared using ammonia-free distilled water. A Sargent water bath and cooler was used in controlled temperature studies. Absorbance readings were made with a Beckman Model OB, spectrophotometer with a 1.0 cm cell at the wavelength of maximum absorbance for the reagent being tested.

For the methyl orange pH 2, DPD oxalate, and phenol red reagents, the tests are performed by adding the sample to a premixed buffer and reagent and determining absorbance at the proper time interval. This order of addition of reagents is necessary for obtaining reproducible results. For the brom cresol purple, phenosafranin, and methyl orange pH 9.5 reagents, the premixed buffer and sample are added to the reagent. This order of addition of reagents keeps bromamine interference at a minimum.

1. Methyl Orange (MO) - pH 2

Methyl orange can be used as a quantitative reagent for total bromine plus free chlorine. If sufficient bromide ion is added, total bromine and chlorine can be determined. The final test pH is 1.8 - 2.15 for samples of 0-1000 mg/1 alkalinity.

This test relies on a bleaching reaction and for this reason, accurate measurement of the reagent is necessary. Also at the low pH required for the test, there are two possible interferences. If the water under test contains bromide ion, chloramine reacts with bromide ion to form bromamine and responds as bromine-bromamine-free chlorine. Bromide is oxidized by chloramine at this pH, and the extent of this reaction depends upon the bromide concentration. If the water contains a high degree of organic pollution, low results for all species may result because of rapid reaction of the halogens with the organics at low pH. In addition such low pH conditions might promote excessive reaction between the free (primarily hypohalous acid species which predominate at low pH levels) and the combined halogens.

The calibration curves at temperatures of 2° to 40°C are linear and cover the range of 0.0 to 4.0 mg/1 of bromine (Figure 1). The M0 test is slightly temperature dependent. Ferric and nitrite ions do not interfere, and interference due to manganic ion may be reduced by use of an arsenite modification. In the 1.5 minutes necessary to determine bromine there is a negligible chloramine interference. However, the presence of bromide ion

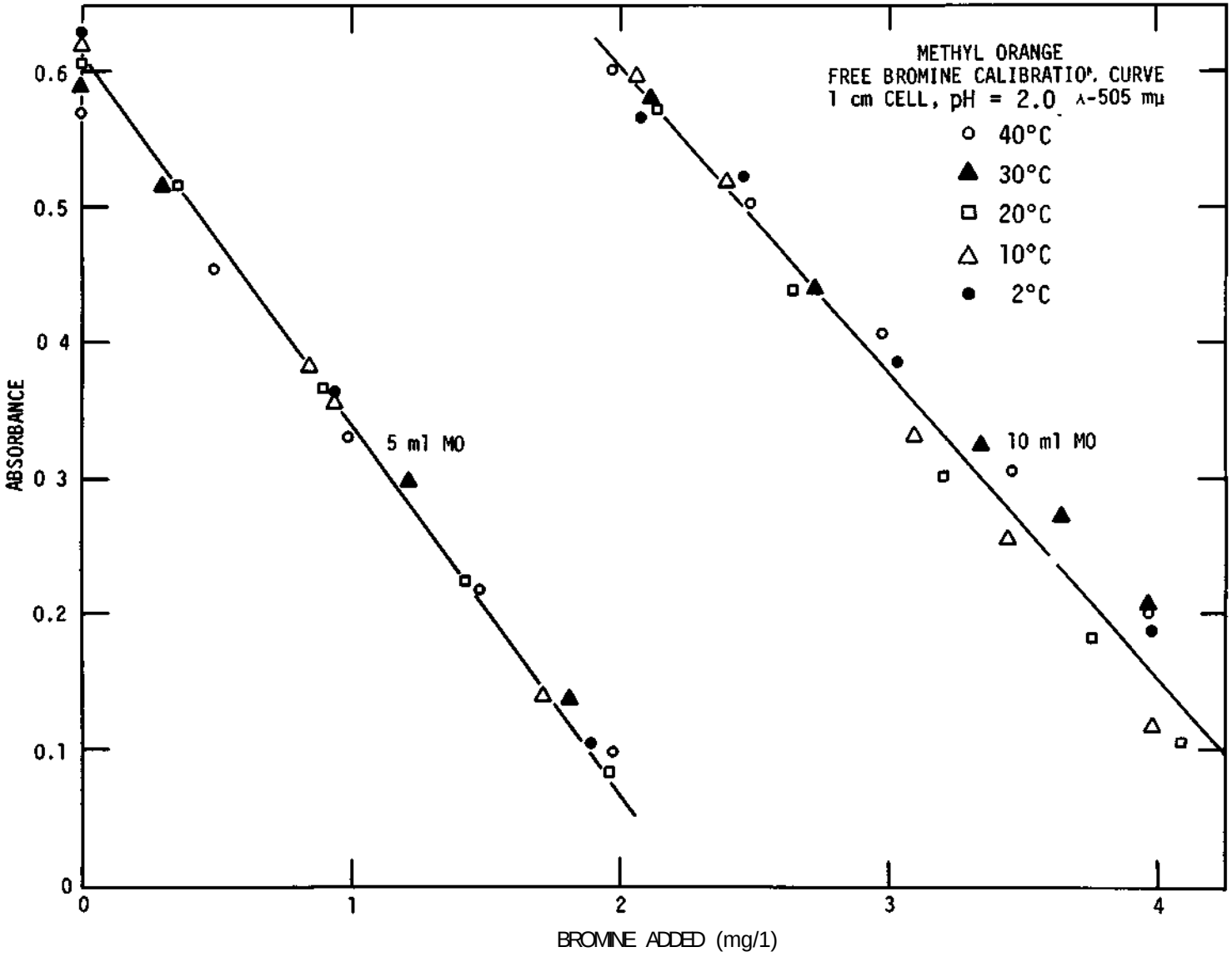
METHYL ORANGE
FREE BROMINE CALIBRATION CURVE
1 cm CELL, pH = 2.0 λ-505 mμ
40°C
30°C
20°C
10°C
2°C
5 ml MO
10 ml MO
ABSORBANCE
0
0.1
0.2
0 3
0 4
0.5
0.6
0
1
2
3
4
BROMINE ADDED (mg/1)

Figure 1

in a sample promotes chloramine reaction, and increasing concentrations of bromide ion increase the rate of reaction of chloramines.

Reagents

(1) Methyl orange: 0.005% methyl orange is prepared by diluting a 0.05% stock solution and adding 1.648 g of sodium chloride per liter of the final dilute solution. This provides a low chloride concentration needed to swamp the effect of chlorides present in the samples. The methyl orange reagent is stable indefinitely.

(2) Chloroacetic acid (practical grade): 91 g of chloroacetic acid diluted to 100 ml.

(3) Bromide: 2.6% solution of sodium bromide

(4) Arsenite-buffer: 0.125 g of sodium arsenite, 14.5 g of sodium citrate, and 0.375 g of citric acid, ground together as a dry powder.

Procedu re

To determine total bromine plus free chlorine, a 50 ml sample is added to 5 ml 0.005% MO containing 1 ml chloroacetic acid solution; this is mixed and the absorbance is determined at 505 mu 1.0-1.5 minutes after preparation. If the absorbance is less than 0.10, the test is repeated using 10 ml 0.005% M0.

If manganese is present, a second determination is required. In this case, 0.10 g of the arsenite-buffer reagent is first dissolved in the 50 ml sample to reduce the residual halogen present. This is then added to the MO-acid mixture and the absorbance is determined at 505 my after 2.5 minutes. The difference in apparent bromine or chlorine concentration found in the first determination and that due to manganese in this determination gives the true residual halogen concentration.

To determine total bromine and chlorine, 0.5 ml of 2.6% sodium bromide solution is added to the sample after the first determination has been completed. The solution is mixed and after 10 minutes the absorbance is again determined. If manganese is present, the above-mentioned correction must be applied.

2. N,N-diethyl-p-phenylene diamine oxalate (DPP)-- pH 6.3

The DPD oxalate test is suitable for the determination of total halogen (total bromine plus total chlorine), if potassium iodide is added to the sample (procedure A).

If certain conditions of sample pH and ammonia concentration are satisfied, then the DPD oxalate test may be used for the determination of total bromine in the presence of free

chlorine and total bromine plus free chlorine (procedures B and C). These conditions which limit the use of the DPD oxalate test will be discussed.

The DPD reaction is a color development reaction in the pH range of 6.2 to 6.5. Therefore, accurate measurement of the quantity of the Indicator is not necessary.

The calibration curve is linear in the range 0.0 to 2.5 mg/1 free bromine, but with an appropriate calibration the range may be extended to 8 mg/1. The calibration curve shows no temperature dependence in the temperature range 2 to 40°C (Figure 2).

Nitrite ion does not interfere with the DPD test. Ferric ion interference Is negligible. Interference due to manganese may be reduced by use of an arsenite modification.

In the 5 minutes contact time before the absorbance is measured, DPD oxalate reacts nearly completely with monobromamine (pH 8.8), dibromamine (pH 7.3) and tribromamine (pH 5) solutions (Figure 3). However, if potassium iodide is not added to the sample prior to the mixing of the solution with the reagent and buffer the DPD response to tri-bromamine Is reduced to about 65 to 70%. Therefore, in the determination of total halogen, potassium iodide crystals are dissolved in the sample prior to testing.

In a further adaptation of Palin's DPD test for chlorine, the chlorine and bromine concentrations may be evaluated separately by the addition of ammonium sulfate to the sample to form halogen amines one minute before the addition of the sample to the DPD reagent. In this way, bromine and bromamine can be determined nearly exclusive of chlorine. However, for samples of pH less than 8 in the presence of low ammonia concentrations, complete response Is not obtained.

Two DPD procedures for total bromine in the presence of chlorine were evaluated: a colorimetric procedure as used in this laboratory for free chlorine determination[1] and Palin's ferrous ammonium sulfate (FAS) titration procedure[2]. With either test, chloramine interferes to some extent. Chloramine interference was greater with the titration procedure; during the one minute required to complete the titration, about 10% of the chloramine present reacted with the DPD, and the continuing chloramine-DPD reaction masked an already indistinct endpoint. Therefore, the DPD colorimetric method is preferred.

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1. T. E. Larson, F. W. Sollo, "Determination of Free Chlorine Residuals in Water," Final Technical Report to the Commission on Environmental Hygiene of the Armed Forces Epidemiological Board, Contract No. DA-49-193-MD-2399, 15 February 1963 to 31 August 1965, p.8.
2. A. T. Palin, "The Determination of Free Residual Bromine in Water," Water and Sewage Works, Vol. 108, p.46l (1961).

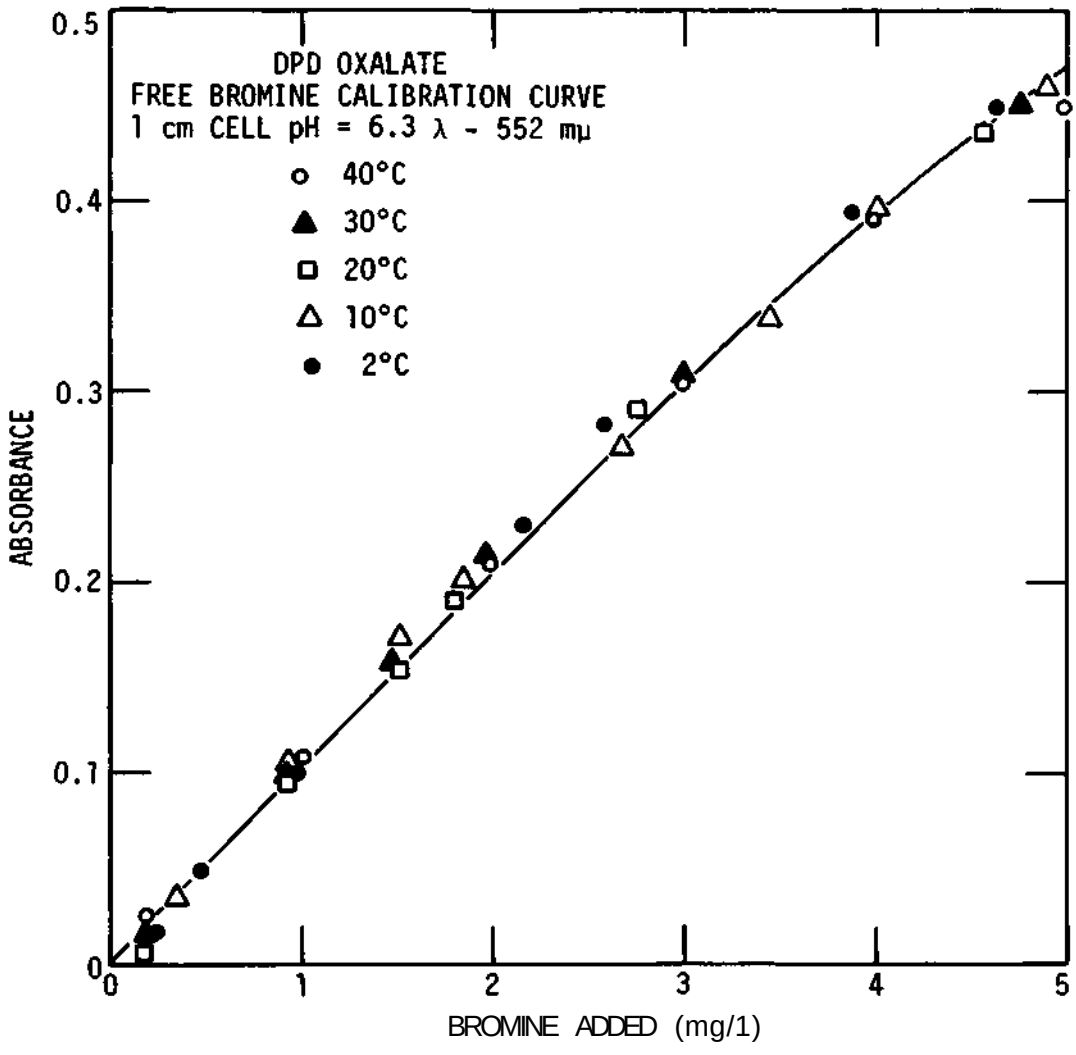
DPD OXALATE
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 6.3 λ - 552 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
BROMINE ADDED (mg/1)

Figure 2

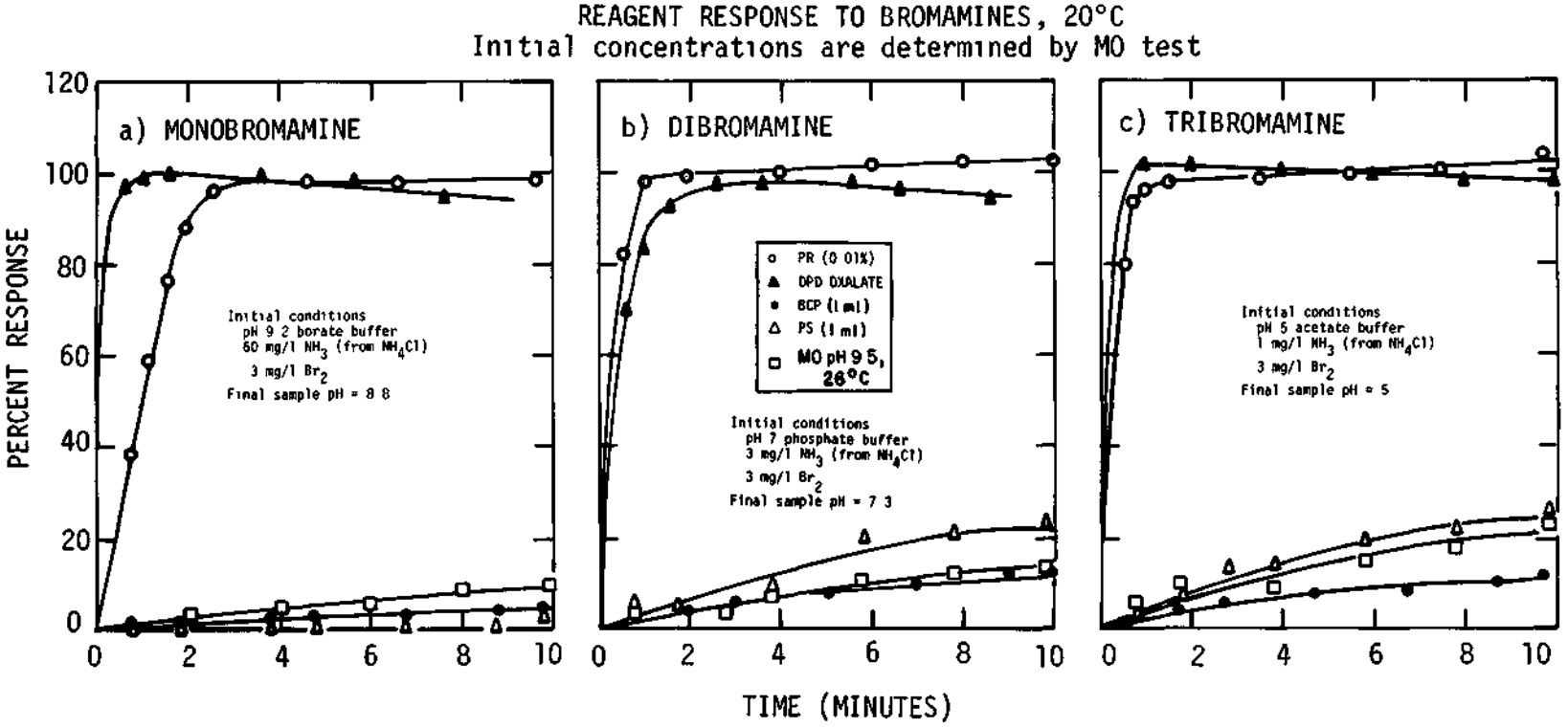
REAGENT RESPONSE TO BROMAMINES, 20°C
Initial concentrations are determined by MO test
a) MONOBROMAMINE
b) DIBROMAMINE
c) TRIBROMAMINE
PERCENT RESPONSE
TIME (MINUTES)
PR (0 01%)
DPD OXALATE
BCP (1 ml)
PS (1 ml)
MO pH 9 5, 26°C
Initial conditions
pH 9 2 borate buffer
60 mg/l NH3 (from NH4Cl)
3 mg/l Br2
Final sample pH = 8 8
Initial conditions
pH 7 phosphate buffer
3 mg/l NH3 (from NH4Cl)
3 mg/l Br2
Final sample pH = 7 3
Initial conditions
pH 5 acetate buffer
1 mg/l NH3 (from NH4Cl)
3 mg/l Br2
Final sample pH = 5

Figure 3

The procedures for total bromine (B) and total bromine plus free chlorine (C) can be used only if the pH of the sample is greater than 8 and ammonia is absent or its concentration is several times that of the total bromine. If these conditions are not satisfied, then procedures B and C are inferior to the test for total halogen (A).

Reagents and procedures for the DPD colorimetric method for total halogen, total bromine, and total bromine plus free chlorine are listed below.

Reagents

(1) DPD oxalate indicator solution: 1 g DPD oxalate is dissolved in ammonia-free distilled water containing 8 ml 1+3 sulfuric acid and 0.2 g disodium ethylenediamine tetraacetate dihydrate (EDTA). This is diluted to 1 liter and stored in an amber glass-stoppered bottle. The reagent, if stored in a refrigerator, can be used for one month.

(2) Buffer pH 6.4: 24 g dibasic sodium phosphate and 46 g monobasic potassium phosphate are dissolved in ammonia-free distilled water. This solution is combined with 100 ml of ammonia-free distilled water, in which 0.8 g EDTA has been dissolved, and then diluted to 1 liter. To this 20 mg mercuric chloride is added.

(3) Potassium iodide, crystal (reagent grade)

(4) Arsenite: 0.5% solution of sodium arsenite

(5) Ammonium sulfate, crystal (reagent grade)

Procedure

(A) To determine tota1 halogen (total bromine plus total chlorine), 1 g potassium iodide is dissolved in 100 ml of sample which is then added, with mixing, to a mixture of 5 ml DPD indicator and 5 ml buffer. The absorbance is determined at 552 my in 5 minutes.

(B) To determine total bromine in the presence of chlorine, 50 mg ammonium sulfate is added to 100 ml of sample, mixed, and allowed to stand for 1 minute. This solution is added to a mixture of 5 ml DPD indicator and 5 ml buffer, and mixed thoroughly. The absorbance is determined at 552 my in 1.5 minutes.

(C) To determine total bromine plus free chlorine, 100 ml of sample is added to a mixture of 5 ml DPD indicator and 5 ml buffer, and mixed thoroughly. The absorbance is determined at 552 my in 1.5 minutes.

If manganese is present, an additional determination is required. interference due to manganese is determined by adding a 100 ml sample with mixing to 5 ml of buffer, 1 potassium iodide crystal, and 0.5 ml of 0.5% sodium arsenite. A 5 ml DPD indicator is then added to this solution with mixing. The absorbance is determined at 552 my after 1.5 minutes. The difference in apparent bromine and/or chlorine concentration found in the original determination and that due to manganese in this determination gives the true residual halogen concentration.

3. Phenol Red (PR)-- pH 5

Phenol red is a unique test for total bromine, free or combined, in concentrations up to 5 mg/1. The reagent is insensitive to free chlorine and chloramine in concentrations up to 6 mg/1 Cl_2. In the 5 minutes contact time before the absorbance is measured, phenol red reacts nearly completely with mono-, di-, and tribromamine solutions (Figure 3).

The bromination of phenol red in the pH range of 4.8-5.0 involves a change of color from yellow to reddish violet depending upon the concentration of bromine. The calibration curve shows no temperature dependence and is linear above 1.5 mg/1 free bromine, but for the lower bromine concentrations it exhibits a decided curvature which may be due to impurities in the reagent (Figure 4). Thus far, attempts to purify the reagent have failed. For low concentrations of bromine (0.2-0.7 mg/1) > accuracy is improved by using a PR reagent of 1/10 the original strength. The PR buffer has the capacity to avoid interference from alkalinity up to 1000 mg/1.

The presence of bromamine may be detected qualitatively in bromine solutions by adding 1 ml of 1% sodium arsenite within 15 seconds after addition of the sample to the phenol red in a second test. If free bromine is the only species present, results of both tests will be the same. If bromamine is present the absorbance of the second test with arsenite will be somewhat less than that without arsenite, because of immediate reduction of the unreacted bromamine.

Reagents

(1) Phenol red reagent solutions:

(a) 0.01% solution-- 10 mg phenol red is dissolved In 1 ml 0.1 N sodium hydroxide and diluted to 100 ml.

(b) 0.001% solution-- 7 drops 0.1 N sodium hydroxide are added to 50 ml of solution (a) and diluted to 500 ml. The phenol red reagent solution is stable for one month.

(2) Buffer pH 5.0: 200 ml 1.0 M sodium acetate and 125 ml 0.8M acetic acid.

(3) Arsenite: 1.0% solution of sodium arsenite

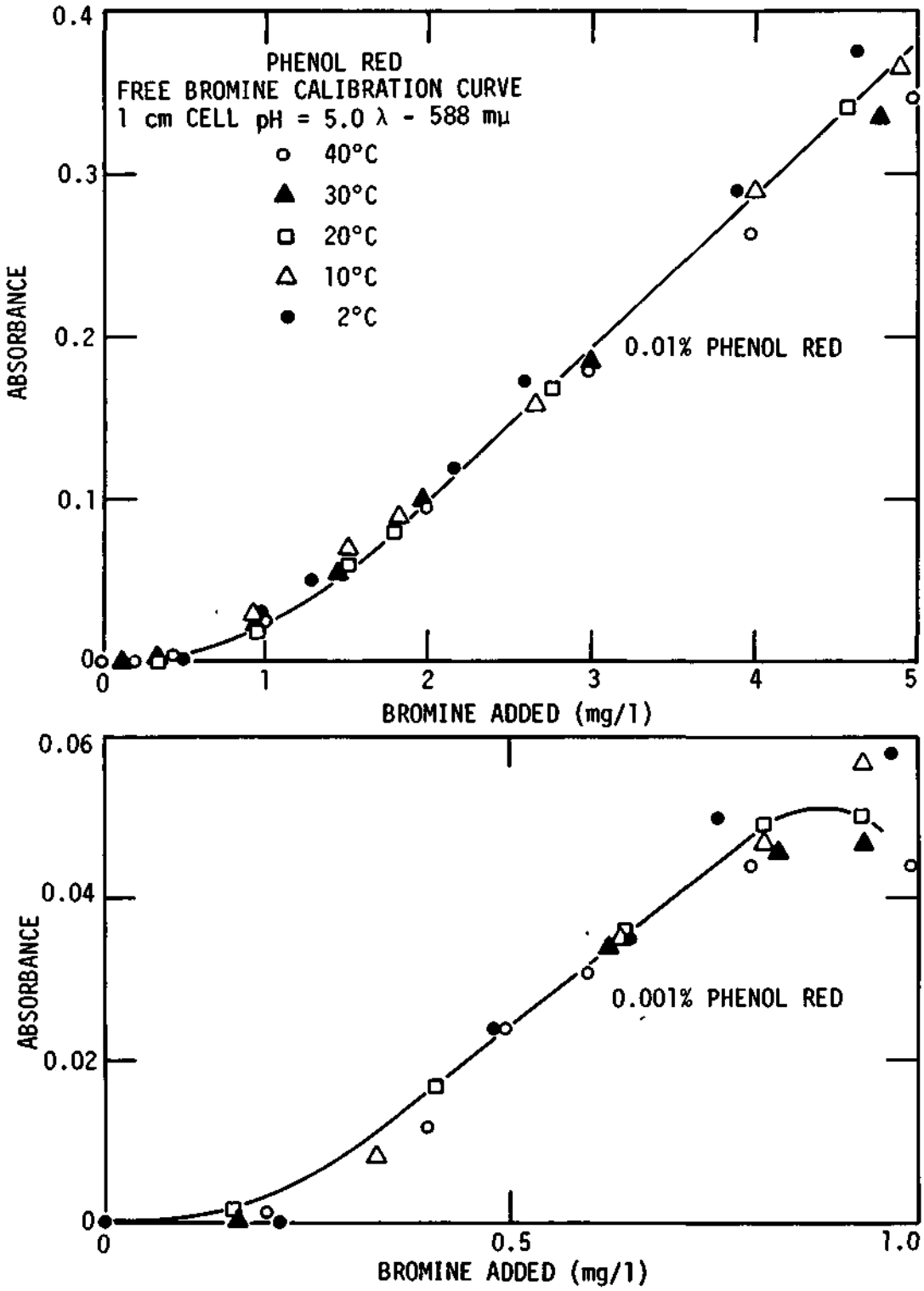
PHENOL RED
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 5.0 λ - 588 mμ
40°C
30°C
20°C
10°C
2°C
0.01% PHENOL RED
ABSORBANCE
BROMINE ADDED (mg/l)
0.001% PHENOL RED
ABSORBANCE
BROMINE ADDED (mg/l)

Figure 4

Procedure

To determine total bromine, a 50 ml sample is added to 2 ml phenol red reagent solution (a) or solution (b) and 5 ml acetate buffer with mixing. After 5 minutes the absorbance is determined at 588 my.

To detect bromamine, the above procedure is repeated, but within 15 seconds after the sample is added to the reagent, 1 ml of 1% sodium arsenite is added. A lower absorbance reading is a qualitative indication of the presence of bromamine.

4. Brom Cresol Purple (BCP)-- pH 9.5

Brom cresol purple reagent is suitable for determining free bromine in concentrations up to 5 mg/1 Br_2. Free chlorine and bromamine interfere only slightly. The BCP response to monobromamine in samples of pH 8.8 is about 1% in 1.5 minutes contact time, and the response to dibromamine (pH 7.3) and tribromamine (pH 5.0) is about 3% in 1.5 minutes contact time (Figure 3).

The BCP test procedure has been changed since the August 1968 Progress Report. Bromamine interference (in particular tribromamine interference) was found to be greater when the sample is added to the premixed reagent and buffer solution. With the new test procedure the premixed sample and buffer are added to the reagent. Figure 3 shows the response of BCP to bromamines using the new test procedure.

The brom cresol purple reaction is based on the bleaching effect of bromine on the reagent at pH 9.5. The BCP buffer has the capacity to avoid interference from alkalinity up to 1000 mg/1. The calibration curve is non-linear below 1 mg/1 free bromine and shows no temperature dependence in the range 2° to 40°C (Figure 5). Accuracy is improved for concentrations between 0.0 and 2.0 mg/1 Br_2 by using 1/3 the quantity of BCP reagent (Figure 6).

In the absence of-bromide ion, free chlorine produces only a slight interference (about 2.5% in 1 min. and 6% in 2 min. contact time). The addition of a solution of sodium arsenite at 1 minute after the sample-buffer-reagent are mixed will further reduce interference due to free chlorine.

Free bromine and free chlorine together can be determined by adding 200 mg/1 bromide ion to the sample before testing. This quantity of bromide ion will be sufficient for sample pH values ranging from pH 4 to 10.

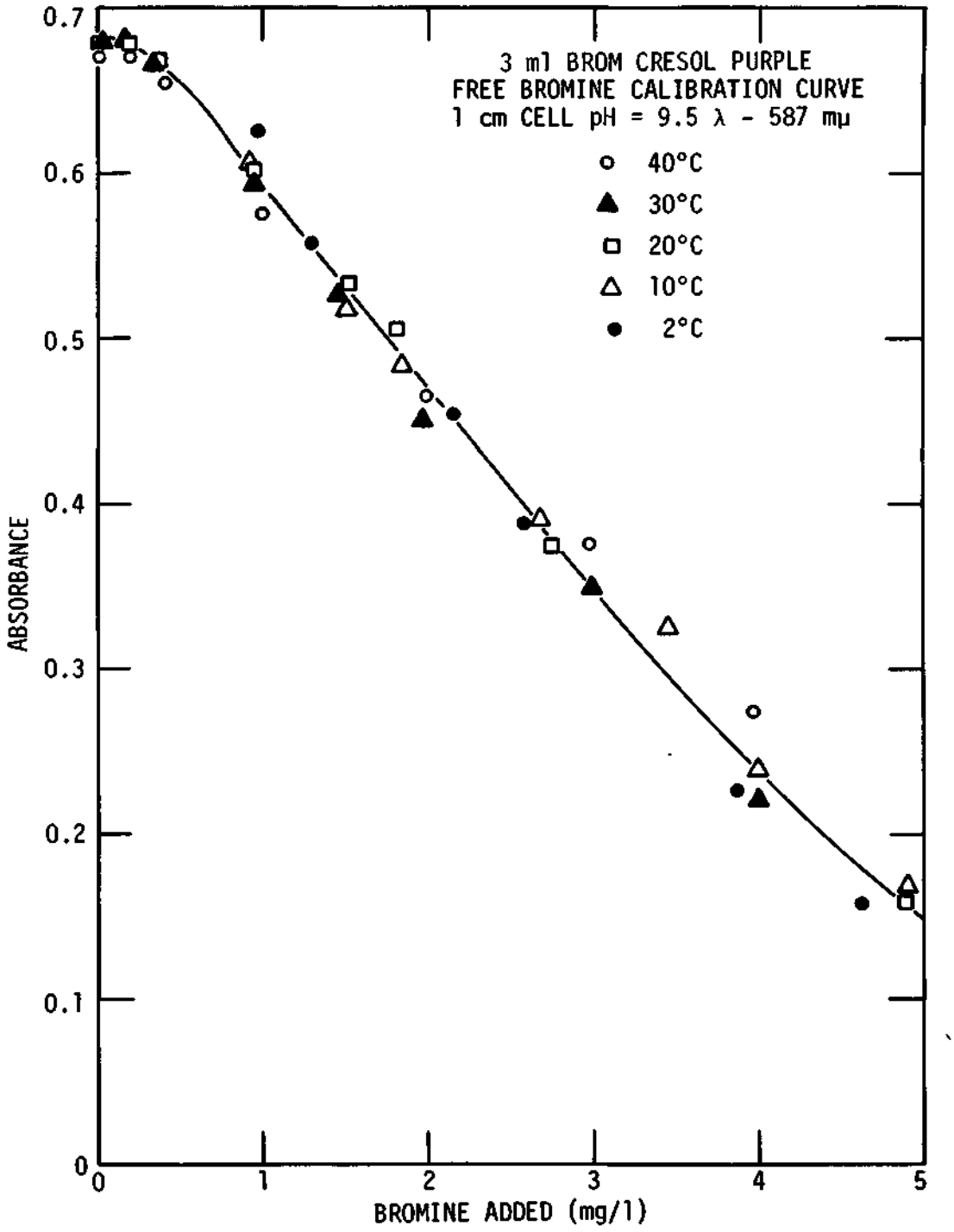
3 ml BROM CRESOL PURPLE
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 587 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
BROMINE ADDED (mg/l)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5

Figure 5

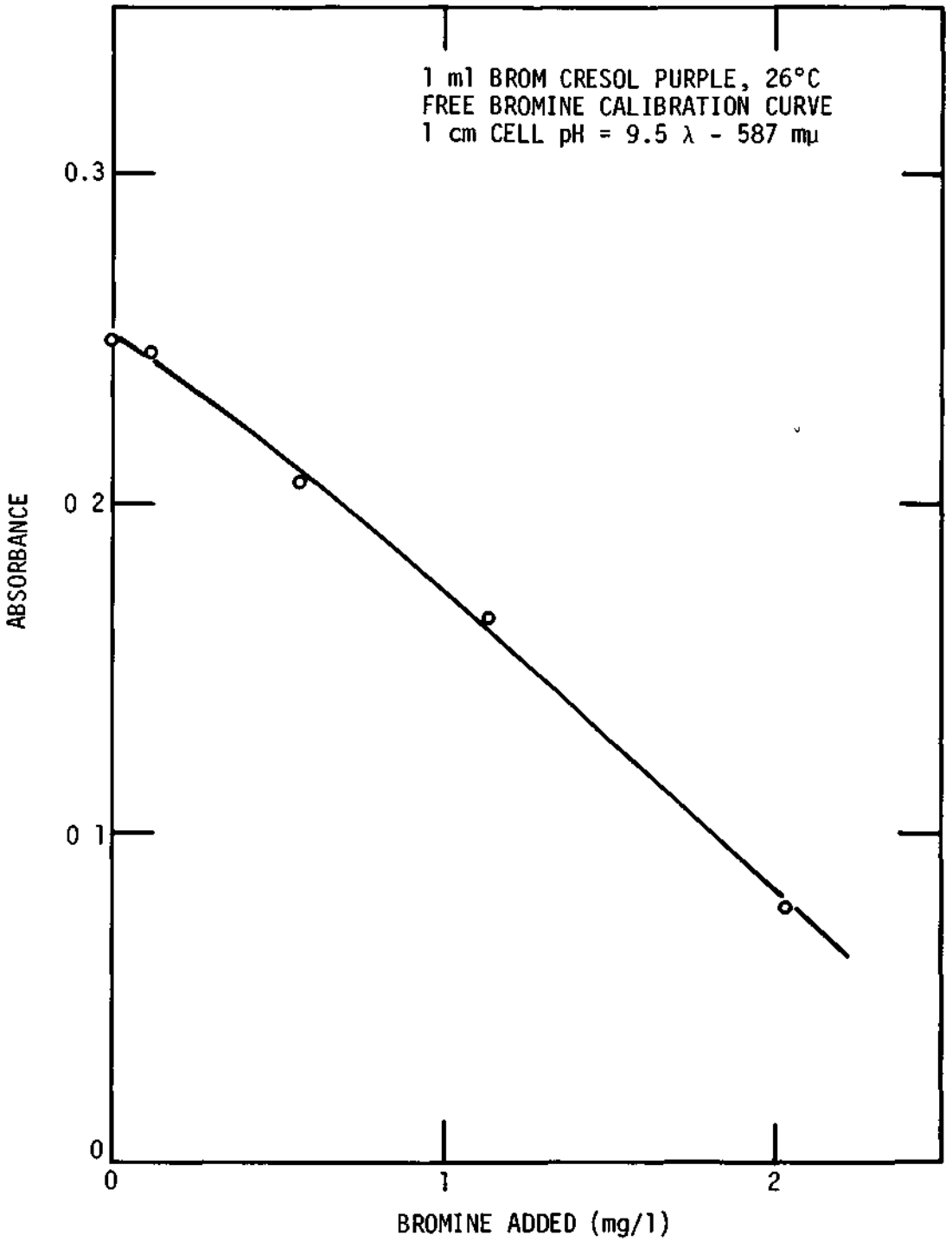
1 ml BROM CRESOL PURPLE, 26°C
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 587 mμ
0.3
0 2
0 1
0
ABSORBANCE
0
1
2
BROMINE ADDED (mg/l)

Figure 6

Reagents

(1) Brom cresol purple, sodium salt: 0.0125% solution (dried at 105°C for 1 hr.) The reagent solution is stable for one month.

(2) Buffer pH 9.5: 0.042 M borax with 6.0 ml 5N sodium hydroxide added per liter.

(3) Arsenite: 1.0% solution of sodium arsenite

(4) Bromide: 2.6% solution of sodium bromide

Procedure

To determine free bromine. a 50 ml sample is added with mixing to 10 ml buffer solution. After 1 minute this solution is added to 1 ml or 3 ml 0.0125% BCP reagent and mixed. At 1 minute, 1 ml 1% sodium arsenite solution is added. The absorbance is determined at 587 mμ after 1.5 minutes.

To determine free bromine and free chlorine together (as Br_2), 0.5 ml of 2.6% sodium bromide is added to a 50 ml sample and thoroughly mixed. The sample is then added to 10 ml buffer, and 1 minute after mixing this solution is added to 1 ml or 3 ml .0125% BCP reagent and mixed. The absorbance is determined at 587 mμ after 1.5 minutes.

5. Phenosafranin (PS)-- pH 9.5

Phenosafranin reagent is suitable for the determination of high concentrations of free bromine. Free chlorine produces a significant interference. Free chlorine interference may be reduced by the addition of a solution of sodium arsenite 15 seconds after the sample-buffer-reagent are mixed. Phenosafranin shows nearly the same type of response to the bromamines as does BCP (Figure 3). In the 1 minute contact time before the absorbance is measured, interference from monobromamine (pH 8.8) is about 1%, that from dibromamine (pH 7.3) is about 3%, and that from tribromamine (pH 5.0) is 5%.

The phenosafranin test procedure and test pH have been changed since the August 1968 Progress Report. Bromamine interference was found to be greater when the sample is added to a premixed buffer-reagent solution. Figure 3 shows the response of phenosafranin to bromamines using the new procedure of adding the premixed buffer-sample solution to the reagent.

The phenosafranin reagent is bleached by bromine at pH 9.5. The calibration curve covers the range 0.0 to 10 mg/1 free bromine and does not appear to be temperature dependent in the range 2 to 40°C (Figure 7). Accuracy is improved for concentrations between 0.0 and 2.0 mg/1 Br_2 by using 1/3 the quantity of PS reagent.

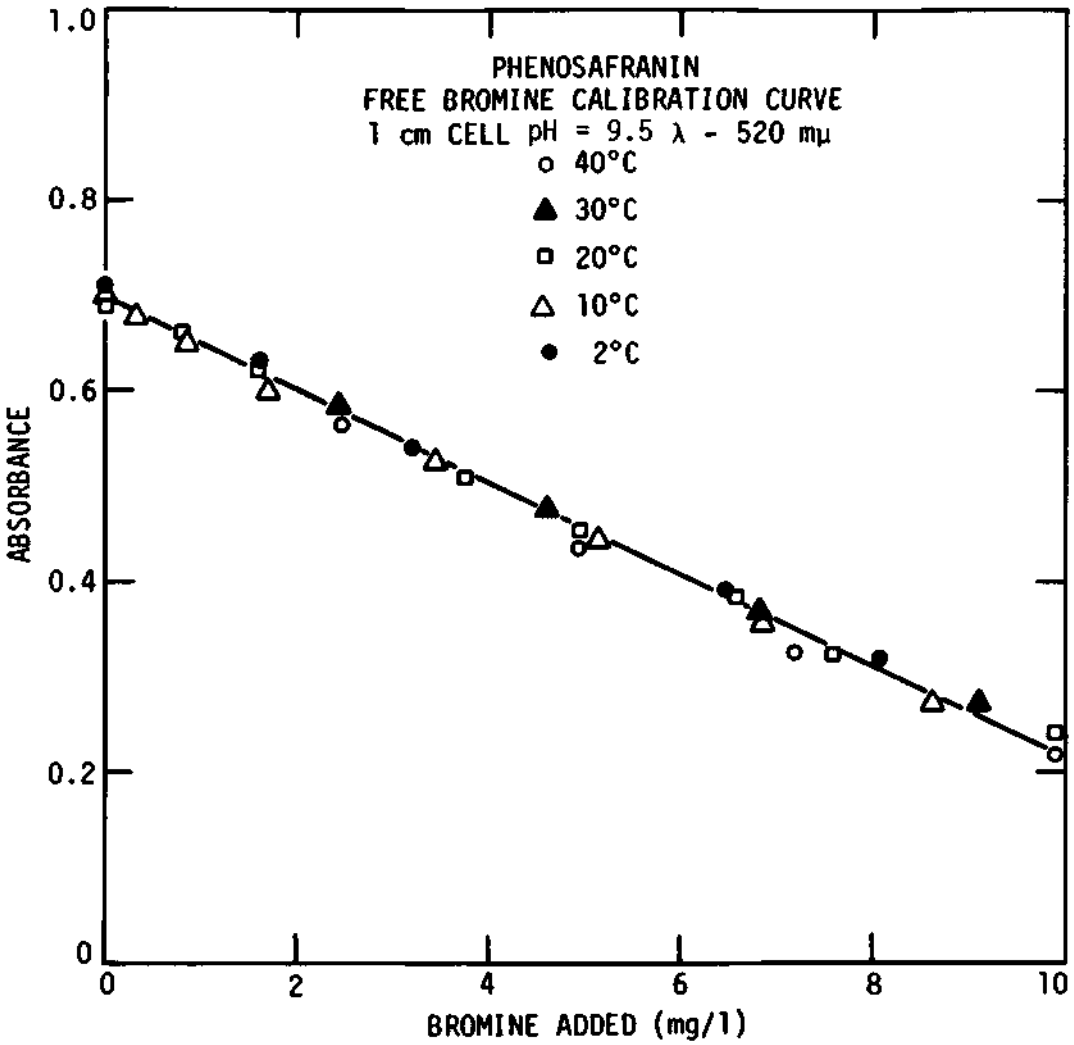
PHENOSAFRANIN
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 520 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
BROMINE ADDED (mg/1)

Figure 7

Reaqents

(1) Phenosafranin: 0.01% solution
The reagent solution is stable for one month.

(2) Buffer pH 9.5: 0.042 M borax with 6.0 ml 5N sodium hydroxide added per liter.

(3) Arsenite: 1.0% solution of sodium arsenite

Procedure

To determine free bromine, a 50 ml sample is added with mixing to 10 ml buffer. After 1 minute this solution is added to 3 ml of 0.01% phenosafranin reagent and mixed. After 15 seconds, 1 ml of 1% sodium arsenite is added and mixed. The absorbance is determined at 520 my within 1 minute.

6. Methyl Orange (MO)-- pH 9.5

Preliminary investigation indicates that at this high pH the methyl orange test is suitable for the determination of free bromine in concentrations up to 6 mg/1 Br_2. Chloramine does not react at this pH, however, interference from free chlorine is significant. Bromamine interference is low.

1.0 mg/1 chloramine (as Cl_2) does not react with methyl orange pH 9.5 and the presence of 200 mg/1 bromide ion does not promote a reaction. However, about 9% of a free chlorine solution reacts in the 1.5 minutes contact time before the absorbance is measured (Figure 8). Free chlorine interference may be reduced by the addition of sodium arsenite one minute after the sample-buffer and reagent are mixed. The response of MO-pH 9.5 to the bromamines is low if the premixed sample and buffer solution is added to the reagent. In the 1.5 minutes contact time before the absorbance is determined, about 3% of a monobromamine solution reacts, about 4% of a dibromamine solution reacts, and about 8% of a tribromamine solution reacts (Figure 3).

The calibration curve is non-linear below 1 mg/1 free bromine (Figure 9). Nitrite ion does not interfere. Ferric ion interferes slightly (Figure 10). Manganese interference has not been examined in detail. To date, all work with this test has been at room temperature (26°C) only.

The M0 test relies on the bleaching effect of bromine on the reagent. Visual color comparisons may be difficult since the test color at pH 9.5 is yellow.

Reagents

(1) Methyl orange: 0.005% methyl orange solution is prepared by diluting a 0.05% stock solution and adding 1.648g of sodium chloride per liter of the final dilute solution. The methyl orange reagent is stable indefinitely.

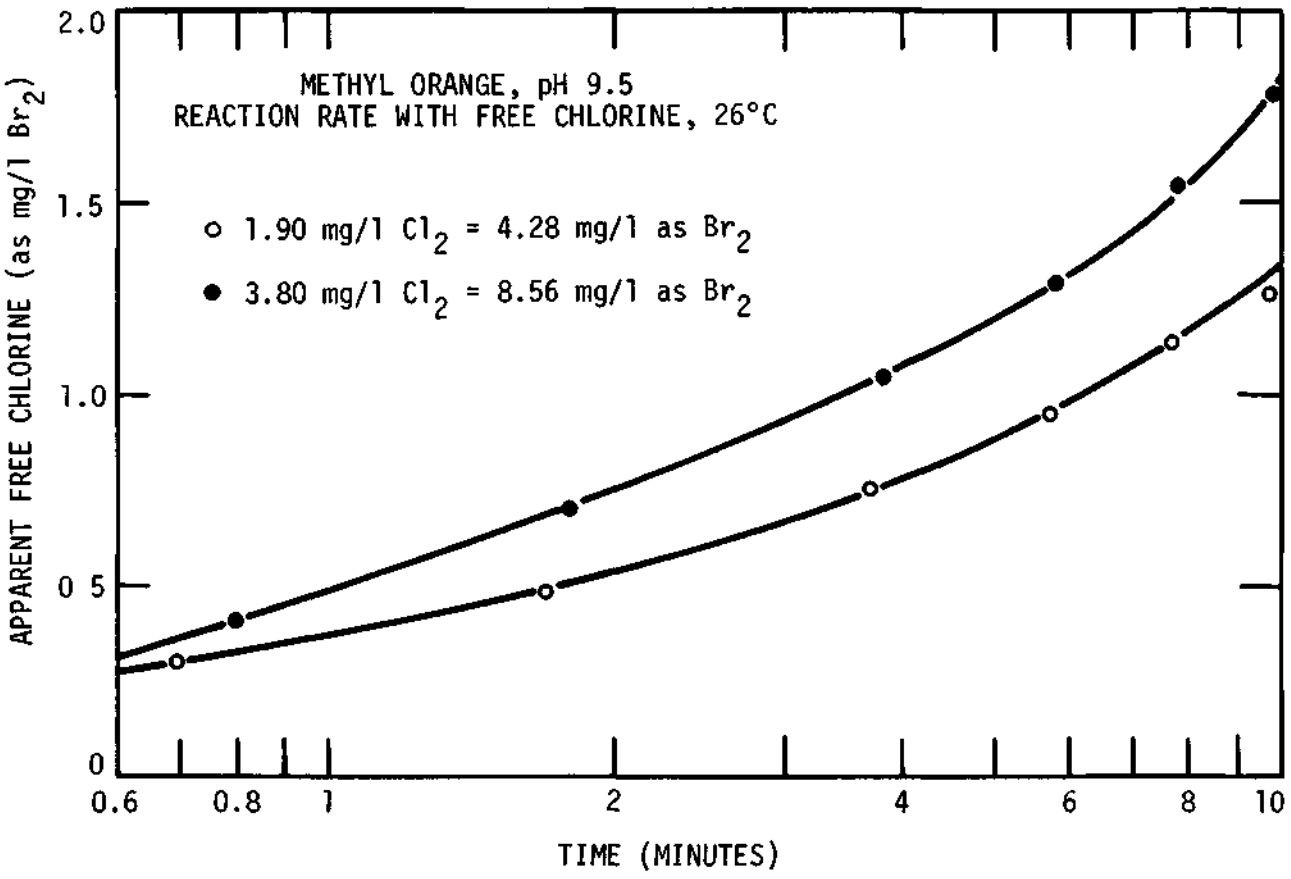
METHYL ORANGE, pH 9.5
REACTION RATE WITH FREE CHLORINE, 26°C
○ 1.90 mg/l Cl_2 = 4.28 mg/l as Br_2
● 3.80 mg/l Cl_2 = 8.56 mg/l as Br_2
APPARENT FREE CHLORINE (as mg/l Br_2)
2.0
1.5
1.0
0 5
0
0.6
0.8
1
2
4
6
8
10
TIME (MINUTES)

Figure 8

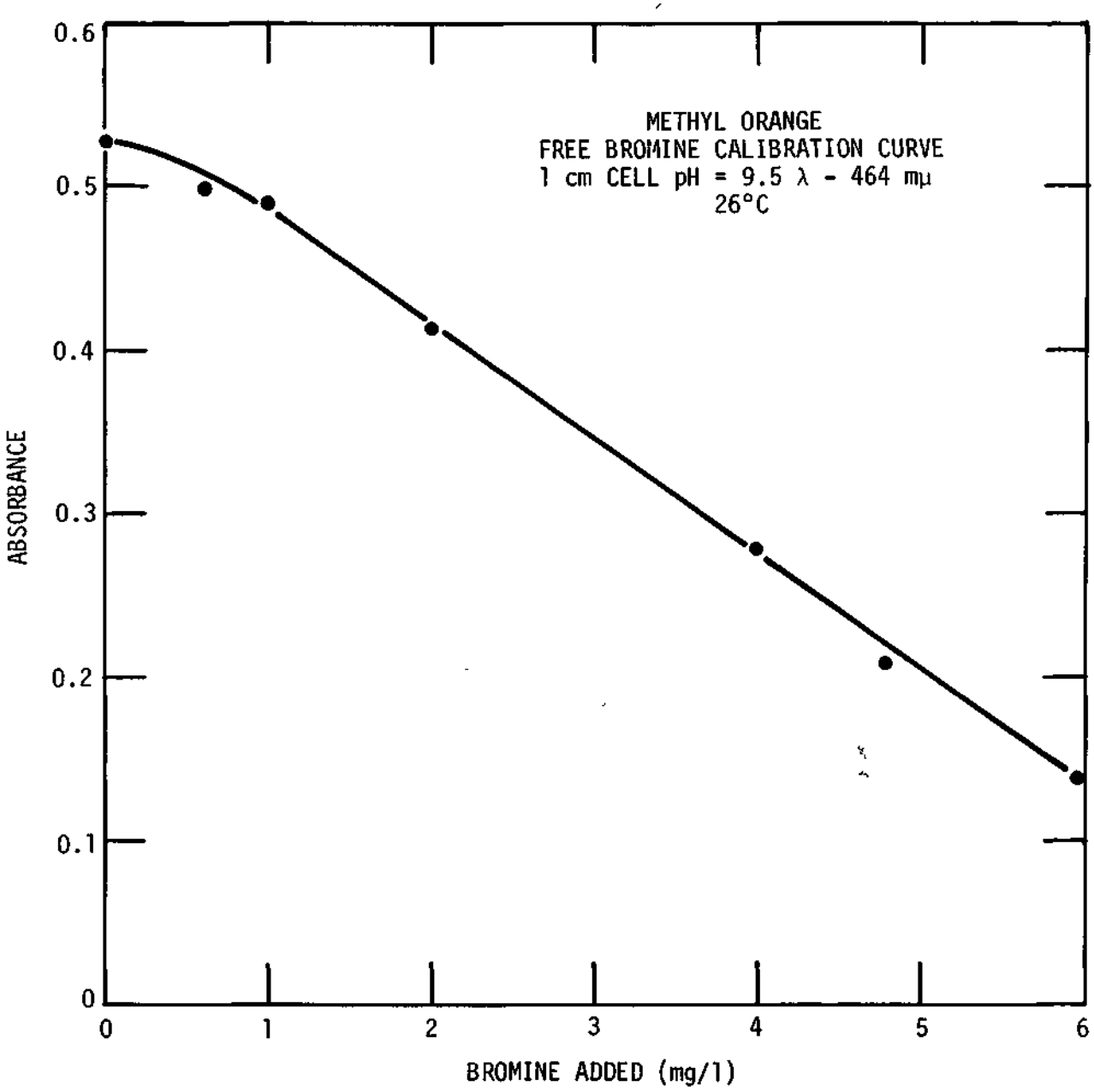
METHYL ORANGE
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 464 mμ
26°C
ABSORBANCE
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
BROMINE ADDED (mg/l)

Figure 9

METHYL ORANGE, pH 9.5 Fe^{+++} Interference, 26°C

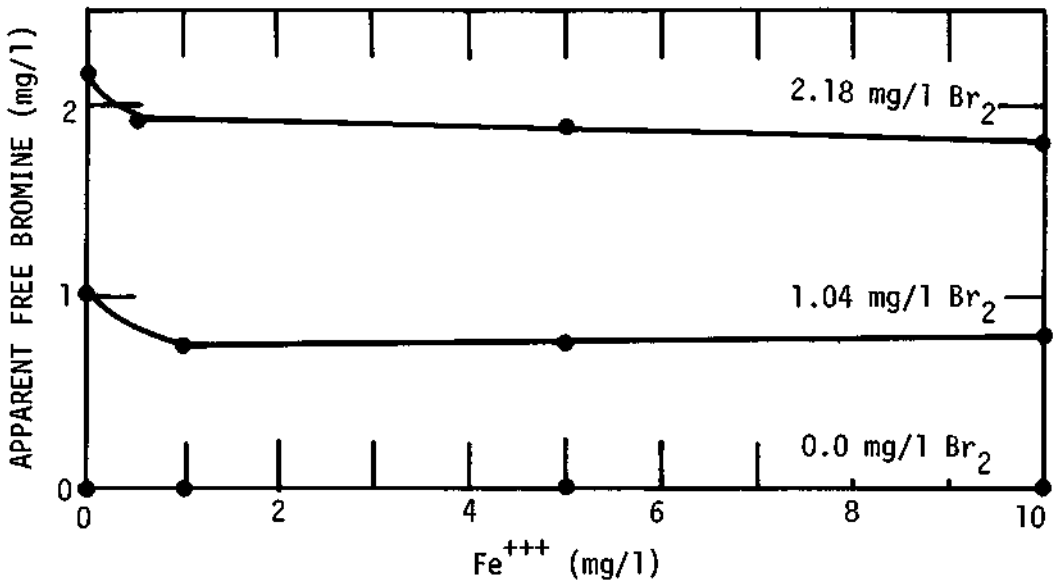

Figure 10

(2) Buffer pH 9.5: 0.042 M borax with 6.0 ml 5 N sodium hydroxide added per liter

(3) Arsenite: 1.0% solution of sodium arsenite

Procedure

To determine free bromine, a 50 ml sample is added, with mixing, to 10 ml buffer. After one minute this solution is added to 10 ml methyl orange and mixed. After one minute 1 ml 1% sodium arsenite solution is added and absorbance is determined at 464 my at 1.5 minutes.

C. An Application of Test Methods-- The Reaction of Chlorine with Buffered Solutions Containing Ammonia and Bromide Ion

Four of the five recommended colorimetric methods have been used for the determination of bromine, bromamine, chlorine, and chloramine In preliminary studies of the reaction of chlorine with solutions containing ammonium and bromide ions. The effect of initial conditions such as pH, ammonium and bromide ion concentrations have been examined in order to determine their relation to the proportion of chloramine and bromamines resulting.

The buffer solutions for the preparation of the samples are listed at the end of this section. 2.0 mg/1 free chlorine was added to buffered samples containing either 0.5 mg/1 or 4 mg/1 ammonia (from ammonium chloride) and bromide ion (from sodium bromide). The bromide ion concentrations were 3, 5, and 25 mg/1. The pH values ranged from 4 to 9. After 2 minutes of contact, aliquots of each sample were removed and the following series of tests were run as nearly simultaneously as possible (Figures 11 and 12).

The brom cresol purple reagent was used to determine free bromine residuals; phenol red was used to determine total bromine only, and methyl orange reagent with bromide added to the final mixture and DPD oxalate with potassium iodide added to the sample were used to determine total halogen (total bromine and total chlorine). The phenosafranin reagent was not tested because its behavior is similar to the brom cresol purple reagent. The methyl orange pM 9.5 test has been added since the completion of this study.

These preliminary studies indicate that the reaction to form bromamines is highly pH dependent. In solutions of $Br^- + NH_3 + Cl_2$, bromamines are formed by a two-step process. Bromide ion must be oxidized by free chlorine before free bromine and ammonia can react. The reaction between free chlorine and ammonia is rapid over the entire range of pH values tested and competes with the reaction between free chlorine and bromide ion. Results indicate that either low pH (below 7) or high concentrations of bromide ion are necessary for appreciable formation of bromamine. With a constant bromide ion concentration, greater concentrations of bromamines are formed at low pH values than at high pH values. Chloramines are the primary species formed at pH values greater

than 7 and do not react with bromide ion unless the pH is reduced to 1ower values.

An examination of the phenol red determination for total bromine, Figures 11 and 12, shows that in the presence of 3 and 5 mg/1 Br^-, negligible quantities of bromamine are formed at sample pH values greater than 7. With 4 mg/1 NH_3 (Figure 12), the lower bromide levels do not respond to chlorination as well as with 0.5 mg/1 NH_3 (Figure 11). However, with 25 mg/1 Br" ion some reaction of chlorine with bromide takes place, and there is, therefore, an increase in the quantity of bromamines formed over the entire range of pH values tested (pH 4 to 9). This reagent isuseful in differentiating between total bromine and tota1 chlorine.

An examination of the HO and DPD determinations for total halogen, Figure 11, shows that at pH 7.4 the concentration of total halogen formed with 0.5 mg/l NH3 in the presence of 25 mg/1 Br" is lower than that formed in the presence of 3 and 5 mg/1 Br". As is noted above, in the presence of 25 mg/1 Br", detectable quantities of bromamines are formed at pH values greater than 7. Apparently, the bromamine species formed at pH 7.4 is predominantly unstable dibromamine. In Figure 12 with 4.0 mg/1 NH3, there appears to be no loss of halogen at the higher bromide leve1.

Buffer Solutions:

(1) Buffer pH 4.3: 100 ml buffer solution contains 9 ml glacial acetic acid and 4.102 g sodium acetate, anhydrous (0.5M).

(0.5 ml buffer was added per 500 ml sample.)

(2) Buffer pH 5.4: 80 ml 0.5M sodium acetate and 16 ml 0.5M acetic acid are combined.

(1 ml buffer was added per 500 ml sample.)

(3) Buffer pH 7.3: 35 g dibasic sodium phosphate and 17 g monobasic potassium phosphate are dissolved in 1 liter ammonia-free distilled water.

(5 ml buffer was added per 500 ml sample.)

(4) Buffer pH 9.2: 0.042M borax

(5 ml buffer was added per 500 ml sample.)

BROMAMINE FORMATION BY CHLORINATION OF NH_3-Br^- SOLUTIONS, 26°C
Initial conditions
0.5 mg/1 NH_3 (from NH_4Cl)
2 mg/1 Cl_2 (=4.5 mg/1 as Br_2)
Bromine residuals were determined after 2 mm. contact time by the MO, DPD, PR, and BCP tests

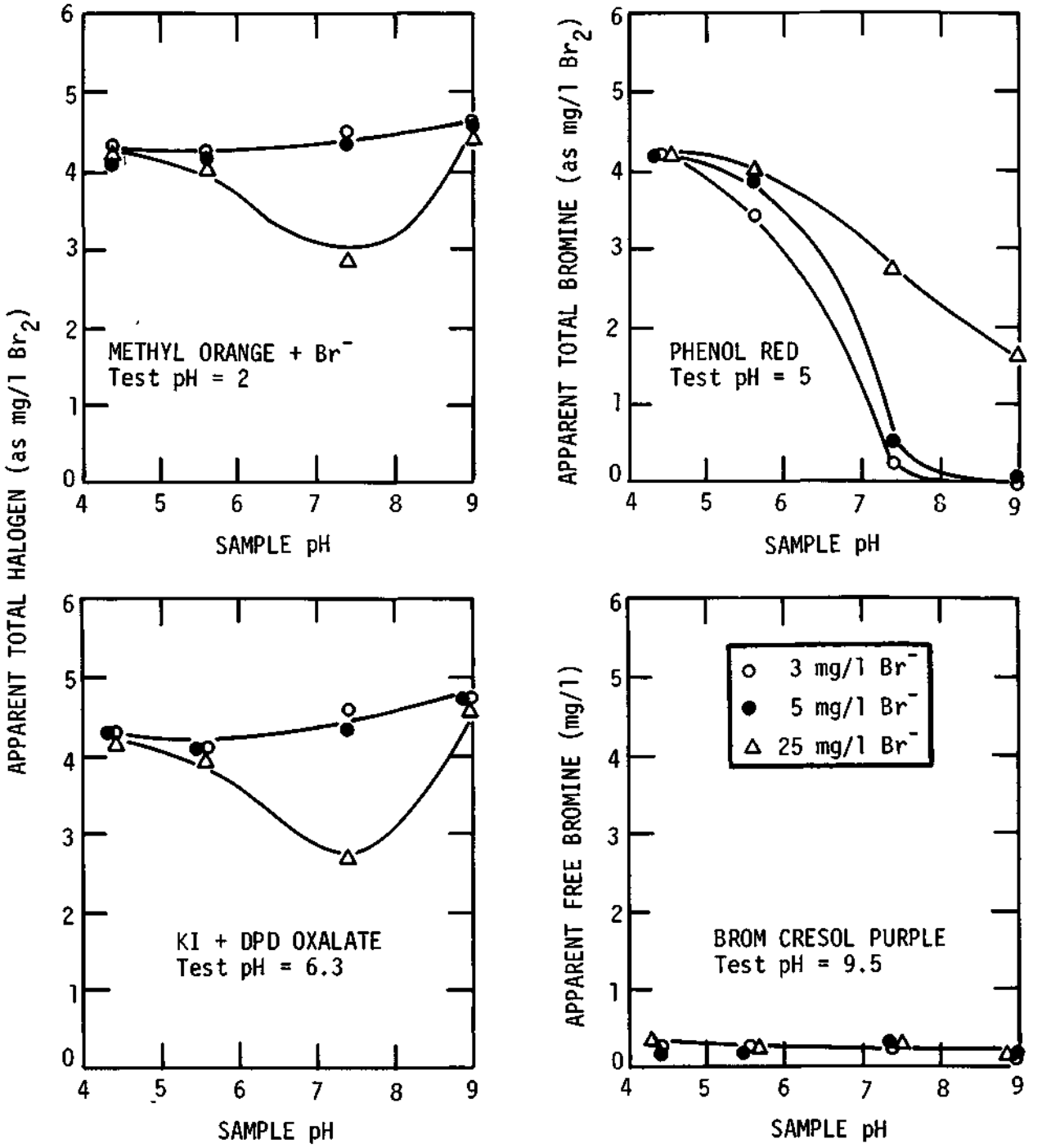

Figure 11

BROMAMINE FORMATION BY CHLORINATION OF NH_3-Br^- SOLUTIONS, 26°C

Initial conditions:
4 mg/l NH_3 (from NH_4Cl)

2 mg/1 Cl_2 (=4.5 mg/1 as Br_2)

Bromine residuals were determined after 2 mm. contact time by the MO, DPD, PR, and BCP tests

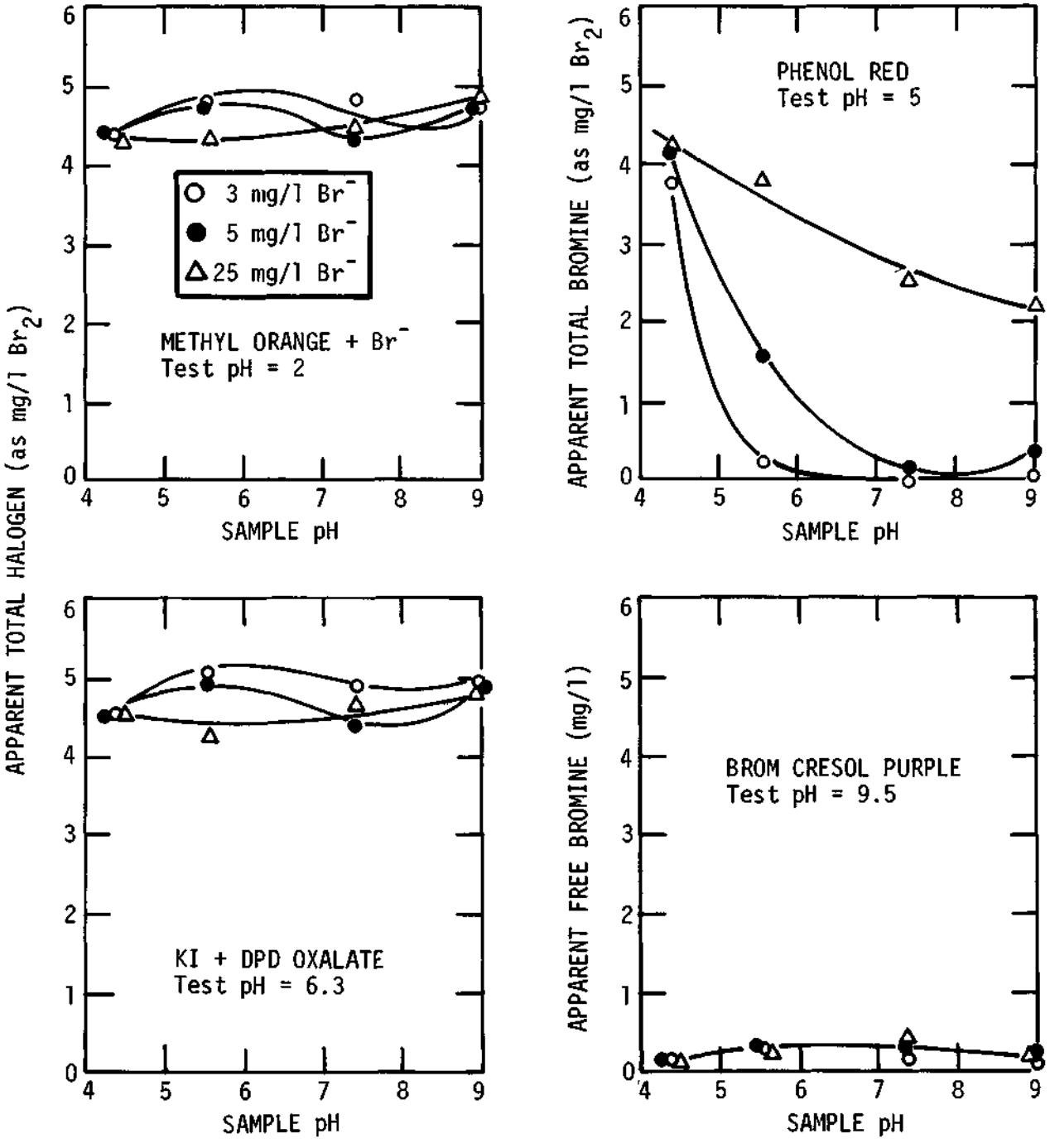

Figure 12

D. Conclusions

In this study twenty-seven reagents have been evaluated for possible use in the determination of free and combined bromine. Ideally, the method should permit the determination of free bromine, free chlorine, bromamines, and chloramines, either when present alone or with other members of this group present. The reason for this requirement is that bromine may be applied by adding a soluble bromide, followed by chlorine or a hypochlorite. Depending upon pH and ammonia content of the water, the result may be a mixture of either free chlorine and bromine or chloramine and bromamine. Distinguishing between free chlorine and free bromine is probably not of the utmost importance, but due to the difference in germicidal activity, it would be necessary to determine bromamine in the presence of chloramine. In addition, the bromine tests were evaluated for stability of reagents, independence of temperature in the range 2 to 40° C, and interference from inorganic compounds (Fe^{+++}, NO_2^-, and Mn^{+++}).

The six colorimetric methods for bromine discussed in this report are listed below with the chlorine and bromine species each can determine.

METHOD	RESIDUALS DETERMINED	TEST pH
Methyl Orange	Cl_2+Br_2+ Bromamine	2.
Methyl Orange + Br^-	Cl_2+Br_2+ Bromamine + Chloramine	2.
DPD Oxalate + Kl (Kl is premixed with sample)	Cl_2+Br_2+ Bromamine + Chloramine	6.3
Phenol Red	Br_2+ Bromamine	5.
Brom Cresol Purple	Br_2	9.5
Phenosafranin	Br_2	9.5
Methyl Orange	Br_2	9.5

Free bromine calibration curves for DPD oxalate, phenol red, brom cresol purple, and phenosafranin do not show temperature dependence. Methyl orange - pH 2 shows a slight temperature dependence in the range 2° to 40°C. Methyl orange - pH 9.5 has been examined only at room temperature (26°C).

Chloramine, ferric, nitrite, and manganic ion interferences are low (when necessary manganese interference can be reduced by an arsenite modification) for the five selected reagents. For the brom cresol purple, phenosafranin, and methyl orange (pH 9.5) reagents monobromamine interference is negligible and di- and tribromamine interferences are low. In the absence of bromide

ion, free chlorine produces significant interference with BCP, PS and MO (pH 9.5) unless sodium arsenite is added after initial mixing.

Methyl orange and DPD oxalate determine total halogen. However, when a high degree of organic pollution is present, the DPD oxalate test is preferred to the MO test because of the higher pH in the test conditions.

The BCP, PR, MO, and DPO oxalate tests were used to study the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide ion.

The brom cresol purple reagent was used to determine the presence of any free bromine. Phenol red determined total bromine only, while methyl orange and DPD can determine total halogen.

Results from this study indicate that the reaction to form bromamines is highly pH dependent. At pH 7 or above, no detectable quantity of bromamine is formed and little loss of chlorine occurs unless the bromide ion concentration exceeds 5 mg/1.

Future work will include a more thorough evaluation of the methyl orange pH 9.5 test for the determination of free bromine. A more detailed study of the reaction of chlorine with solutions containing ammonia and bromide ion is needed. Perhaps the effect of varying contact times and temperature should be determined. The six recommended test methods will be evaluated for their performance in highly polluted water.

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13 ABSTRACT

The major objective of this work has been the development of suitable methods for the determination of free bromine and bromamines in water, with emphasis on methods that would be suitable for field use. A number of reagents were screened on the basis of their reaction with H0C1, HOBr, NH_2Cl, and NH_2Br. Six reagents -- methyl orange pH 2, DPD oxalate, phenol red, brom cresol purple, phenosafranin, and methyl orange pH 9.5 -- were selected for detailed investigation.

These six methods have been examined for response to mono-, di-, and tribromamine. Test procedures for DPD, brom cresol purple, and phenosafranin have been changed slightly. To promote the complete reaction of bromamines with DPD oxalate, potassium iodide is added to the sample prior to testing. To keep bromamine interference at a minimum for the brom cresol purple and phenosafranin tests, the premixed sample and buffer are added to the reagent.

The methyl orange pH 2, DPD, phenol red, and brom cresol purple tests were used to study the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide ion. The reaction to form bromamines depends primarily upon pH.

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Water						
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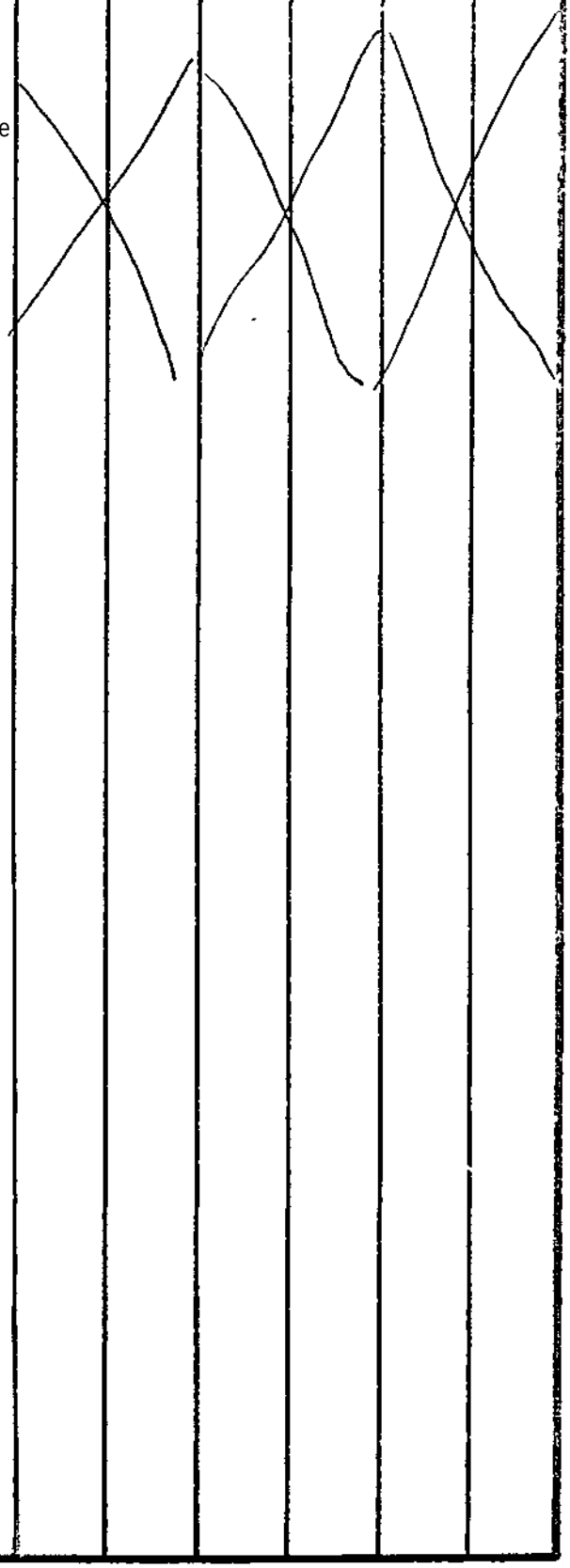
Bromine						
Methyl Oranqe						
N,N-diethyl-p-phenylene diamine Oxalate						
Phenol Red						
Brom C resol Purple						
Phenosafranin						



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