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DETERMINATION OF FREE BROMINE IN WATER (U)

ANNUAL PROGRESS REPORT

by

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August 1968

(For the period 1 July 1967 to 30 June 1968)

Supported by

U.S. ARMY MEDICAL RESEARCH 6 DEVELOPMENT COMMAND
Office of The Surgeon General, Washington, D.C. 20315
in cooperation with the Commission on Environmental Hygiene
of the Armed Forces Epidemiological Board

Contract No. Da-49-193-MD-2909
Illinois State Water Survey
Urbana, Illinois 61801

I. SUMMARY

The four selected colorimetric reagents, methyl orange, phenol red, brom cresol purple, and phenosafranin, have been evaluated in waters containing ammonia and amino acids. In general, brom cresol purple and phenosafranin were in good agreement for the free bromine determinations, and methyl orange and phenol red were in fairly good agreement for the total residual bromine determinations.

In a study of the disinfection of activated sludge effluents, it was found that both acid ortho-tolidine and methyl orange produced low results in the determination of total available chlorine, whereas DPD gave values in better agreement with amperometric titration values. It appears probable that this effect will also be found with bromine in highly polluted waters, and for this reason DPD will be included in future evaluations.

Studies made on the stability of the phenol red, brom cresol purple, and phenosafranin reagent solutions, indicate that the three reagents are stable for four weeks but should not be used thereafter.

Studies on the chlorination of solutions containing ammonia and bromide ion indicate that bromamine formation is dependent upon pH and bromide concentration and possibly upon ammonia concentration. At pH 7 or above, no detectable quantity of bromamine is formed and no loss of chlorine occurs unless the bromide ion concentration exceeds 5 mg/1.

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IV. DETERMINATION OF FREE BROMINE IN WATER

A. Introduction

The purpose of this project is to develop a method for the determination of bromine and bromamines in water, with emphasis on methods that would be suitable for field use. As previously reported, twenty-seven reagents were evaluated for possible use as colorimetric tests for free bromine .

Four reagents were selected for detailed investigation, primarily because interferences due to chloramine, ferric ion, nitrite ion, and manganese are low (though none is free of all interference). The four reagents and the species each can determine are:

1. methyl orange - tota1 residual bromine and free ch1orine,
2. phenol red - tota1 bromine,
3. brom cresol purp1e - free bromine and chlorine,
4. phenosafranin - high concentrations of free bromine.

Recently, the N,N-diethy1-p-pheny1ene diamine oxalate colorimetric test has again been considered for the determination of total residual bromine in the absence of chlorine.

The DPD oxalate and the methyl orange tests have been compared in determining the effect of pH on the stability of bromamine solutions and show good agreement.

A study was made of the reaction of chlorine with solutions containing ammonia and bromide ion. The pH of the solutions was varied. The results indicate that a high concentration of bromide ion or low pH is necessary for the formation of bromamine.

The four colorimetric tests, brom cresol purple, phenosafranin, phenol red, and methyl orange,have been evaluated in water containing ammonia and amino acids. Free residual bromine values determined by BCP and phenosafranin were in good agreement. Agreement between MO and PR tests for total residual bromine at higher levels In the absence of chlorine was satisfactory.

In all figures the data are indicated in terms of the halogen employed, except where both halogens were present In which case the results are as apparent bromine.

B. EVALUATION OF TEST METHODS

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

1. Methyl Orange (MO)

The methyl orange test is suitable for the determination of total residual bromine in waters containing no chlorine or total residual bromine plus free chlorine. Addition of an excess of bromide ion to the sample promotes a rapid quantitative reaction of chloramine with methyl orange at pH2, the final pH for this method.

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 MO test is slightly temperature dependent. Ferric and nitrite ions do not interfere, and interference due to manganic ion may be eliminated 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 in a sample promotes chloramine reaction and increasing concentrations of bromide ion increase the rate of reaction of chloramines.

Reagents :

(1) 0.005% methyl orange is diluted from a 0.05% stock solution, with 1.648 g sodium chloride added per liter of final solution. This provides a low chloride concentration needed to swamp the effect of chlorides present in the samples.

(2) 91% chloroacetic acid (practical grade) - 91 g chloroacetic acid diluted to 100 ml

(3) 2.6% sodium bromide

Procedure :

To determine total residual bromine plus free ch1orine, a 50 ml sample is added to 5 ml 0.005% M0 containing 1 ml chloroacetic acid solution; this is mixed and absorbance is determined 1.0-1.5 minutes after preparation at 505 my, pH 1.9. If the absorbance is less than 0.10, the test is repeated using 10 ml 0.005% methyl orange.

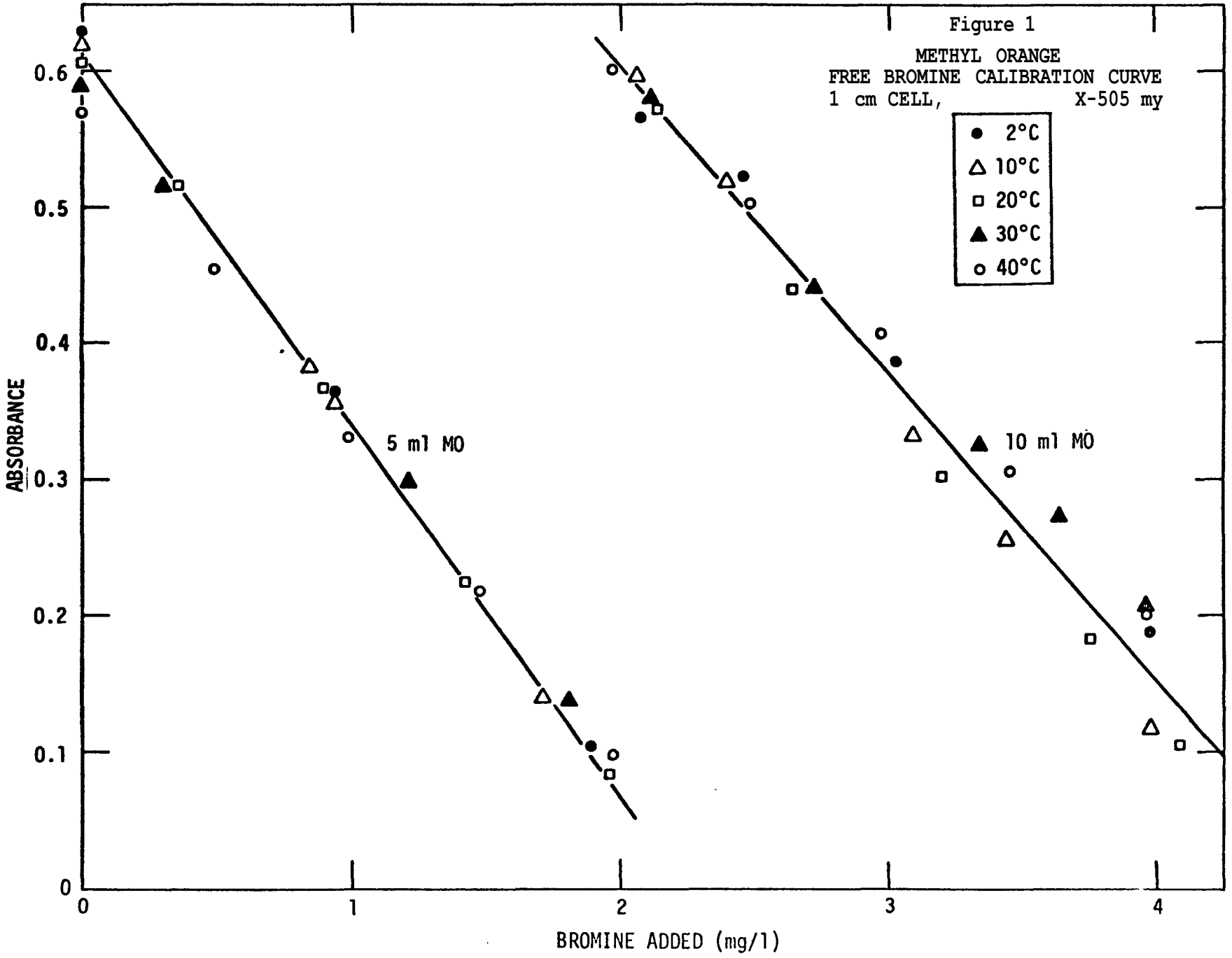
Figure 1
METHYL ORANGE
FREE BROMINE CALIBRATION CURVE
1 cm CELL, X-505 my
2°C
10°C
20°C
30°C
40°C
5 ml MO
10 ml MO
ABSORBANCE
BROMINE ADDED (mg/l)
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3
4

To determine total residual 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 absorbance is less than 0.10, a new sample should be prepared using a larger quantity of methyl orange.

2. Phenol Red (PR)

The phenol red test is suitable for the determination of total residual bromine with no interference from free or combined chlorine. Free bromine reacts almost instantaneously, whereas combined bromine requires two minutes or more for complete reaction at temperatures in the range of 2° to 40°C.

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 separate test. If free bromine is the only species present, both results will be the same. If bromamine is present the absorbance of the second test with arsenite will be somewhat less than that without arsenite, due to immediate reduction of the unreacted bromamine.

The calibration curve (figure 2) for phenol red is non-linear at low bromine concentrations. With the usual 0.01% reagent, the test is not sensitive to concentrations of bromine less than about 0.5 mg/1. For concentrations from 0.2 to 0.7 mg/1, a 0.001% reagent was used with some improvement in linearity (figure 2), but a cell length of 5 or 10 cm would be desirable to permit greater accuracy.

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. The phenol red reagent solution (0.01%) is stable for one month only.

   (b) 0.001% solution - to 50 ml of solution (a) is added 7 drops 0.1 N sodium hydroxide and diluted to 500 ml.

(2) Buffer pH 5.1 - 200 ml 0.5 M sodium acetate and 125 ml 0.4 M acetic acid.

(3) 1.0% sodium arsenite

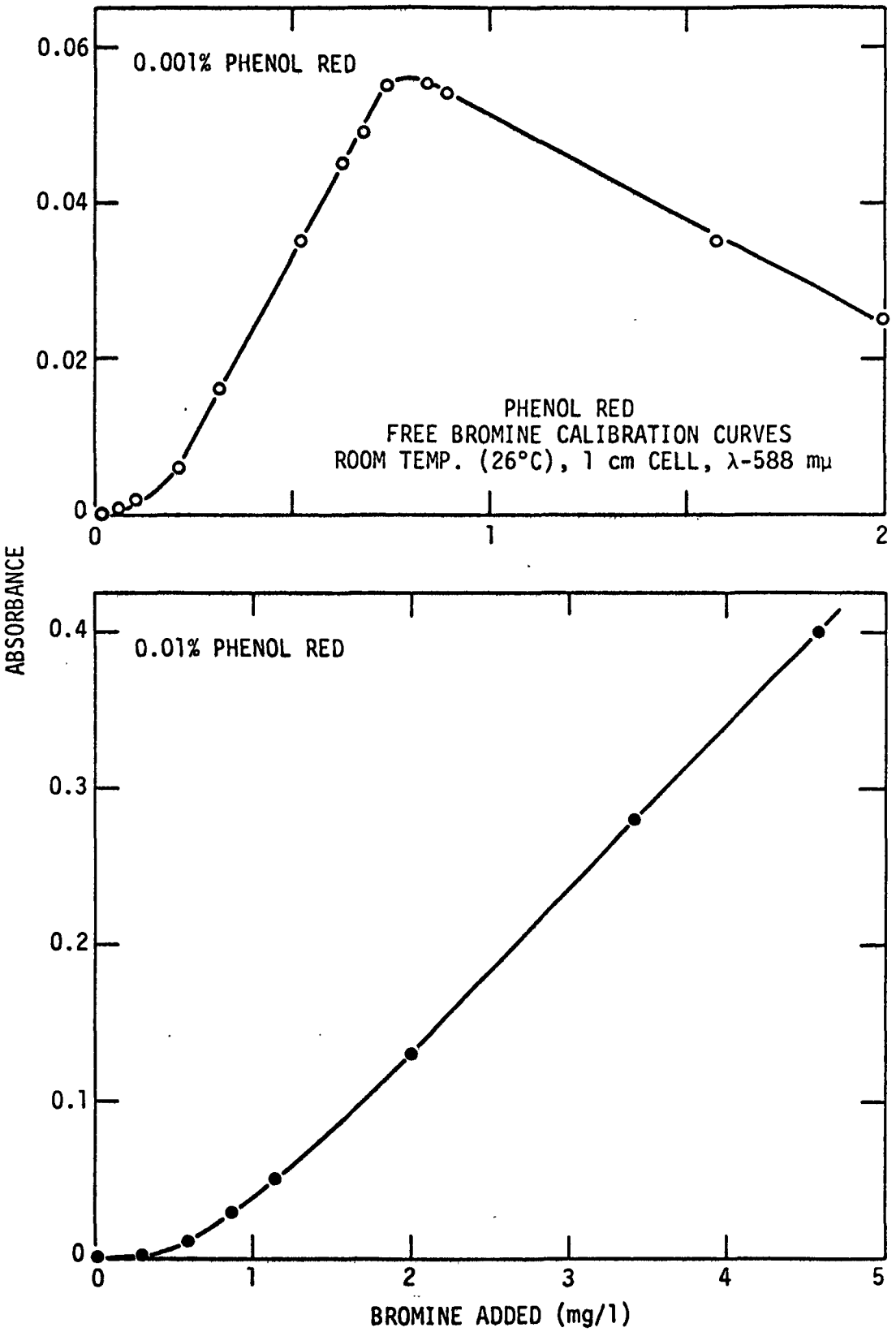
0.001% PHENOL RED
PHENOL RED
FREE BROMINE CALIBRATION CURVES
ROOM TEMP. (26°C), 1 cm CELL, λ-588 mμ
0.01% PHENOL RED
ABSORBANCE
BROMINE ADDED (mg/l)

Figure 2

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, pH 5.1.

To detect bromamine, the procedure above 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 in this second test indicates the presence of bromamine.

3. Brom Cresol Purple (BCP)

The brom cresol purple calibration curve (figure 3) is non-linear, particularly at concentrations below 0.50 mg/1 Br2. The curve covers the range 0.0 to 4.5 mg/1 Br2. A new buffer having a greater buffering capacity is being used for the brom cresol purple test.

Brom cresol purple is nearly specific for free bromine with interference only from free chlorine. Neither monobromamine or monochloramine interfere.

At room temperature (26) approximately 40% of the free chlorine present reacts with brom cresol purple within 10 minutes as shown in figure 4. The addition of sodium arsenite within 15 seconds after the sample is added to the reagent-buffer mixture will reduce free chlorine interference to negligible quantities if no free bromine is present. However, in solutions containing free bromine plus free chlorine the chlorine reacts with the BCP reagent at the rate of approximately 4% for every 15 seconds of delay before the addition of sodium arsenite. With bromine present, at least 30 seconds must be allowed before adding the arsenite to obtain full response with the bromine. The following is an example of this:

mg/l Br_2 added	mg/l Cl_2 added	apparent mg/1 recovered as free bromine		
		15 sec.*	30 sec.*	60 sec.*
2.92	0.0	2.78	2.98	2.91
0.0	3.56	0.20	0.23	0.35
2.92	3.56	3.37	3.92	4.49

(3.56 mg/1 Cl_2 = 8.01 mg/1 as Br_2)

* Time interval before addition of arsenite

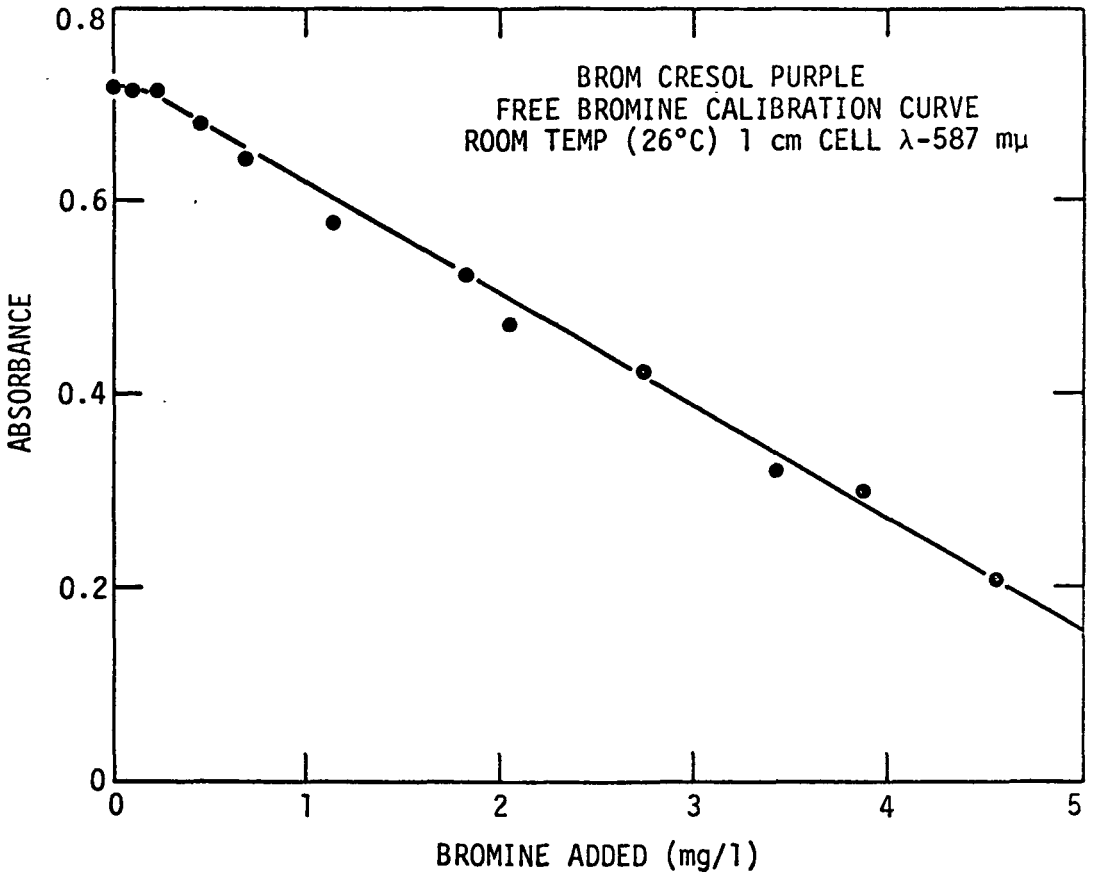
BROM CRESOL PURPLE
FREE BROMINE CALIBRATION CURVE
ROOM TEMP (26°C) 1 cm CELL λ-587 mμ
ABSORBANCE
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
BROMINE ADDED (mg/l)

Figure 3

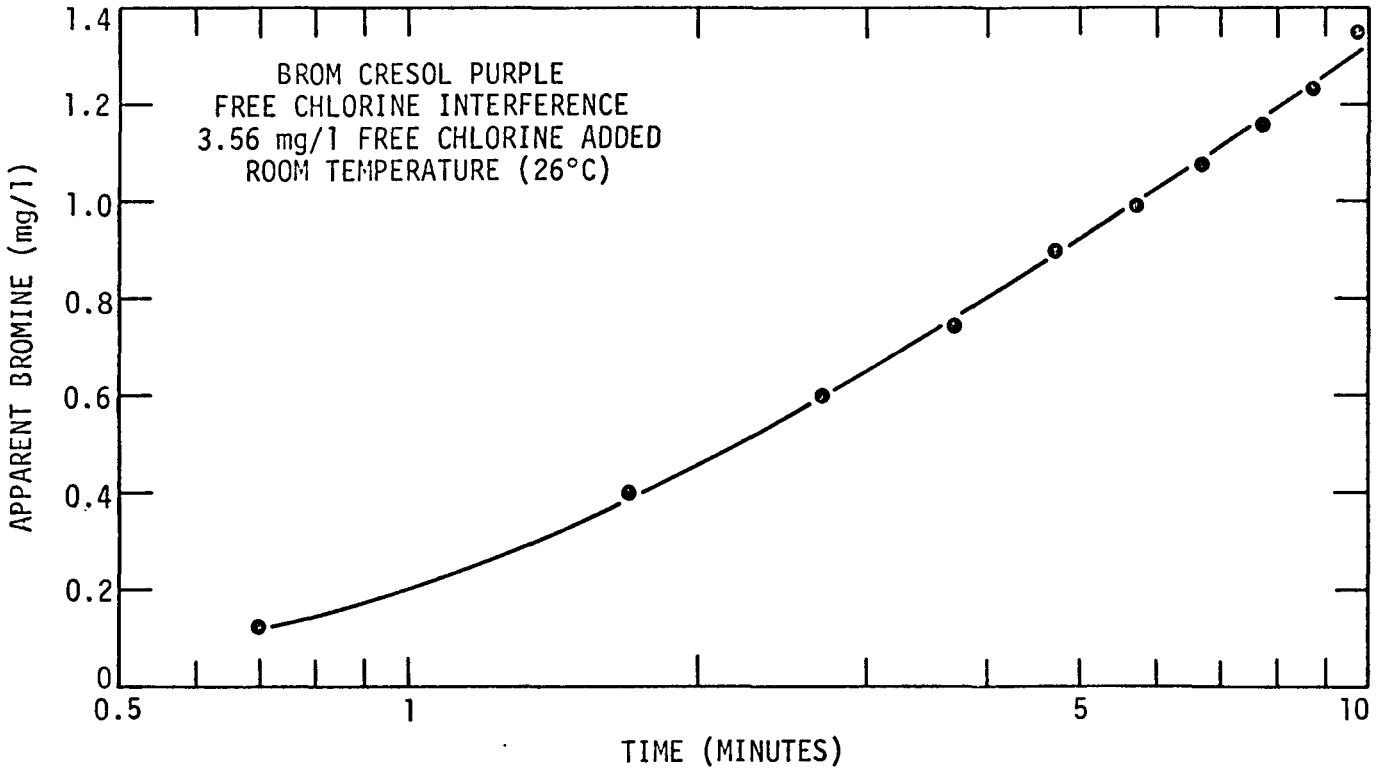
BROM CRESOL PURPLE
FREE CHLORINE INTERFERENCE
3.56 mg/l FREE CHLORINE ADDED
ROOM TEMPERATURE (26°C)
APPARENT BROMINE (mg/l)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.5
1
5
10
TIME (MINUTES)

Figure 4

This effect is probably due to the bromide ion in the bromine solution which is slowly oxidized by the chlorine.

Free bromine and free chlorine together can be determined by adding 200 mg/1 bromide ion to the sample before testing.

Reagents;

(1) 0.0125% brom cresol purple, sodium salt- (Dried at 103°C for 1 hr.). The BCP reagent solution is stable for 1 month only.

(2) Buffer solution (pH 94.) - 0.042 M borax with 6.0 ml 5N sodium hydroxide added per liter.

(3) 2.6% sodium bromide

(4 1.0% sodium arsenite

Procedure:

To determine free bromine, a 50 ml sample is added with mixing, to 3 ml of 0.0125% BCP and 10 ml of buffer solution. After 1 minute 1 ml sodium arsenite is added and the solution is mixed well. The absorbance of the resulting solution is determined at 587 my, pH 9.3.

To determine the free bromine and free chlorine together, 0.5 ml 2.6% sodium bromide solution is added to a 50 ml sample and thoroughly mixed. The sample is then added, with mixing, to 3 ml 0.0125% BCP and 10 ml buffer, and after 1 minute the absorbance is determined at 587 mu, as before.

4. Phenosafranin

The phenosafranin test may be used for the determination of free bromine. The reaction between free bromine and phenosafranin does not appear to be temperature dependent in the range 2° to 40°C (figure 5). The curve covers the range of 0.0 to 10 mg/1 Br_2. Because of its rather low sensitivity with a 1 cm cell, this reagent has 1imited value.

Bromamine and free chlorine react slowly with phenosafranin but the addition of 1 ml of 1% sodium arsenite within 15 seconds after the sample is added to the reagent will eliminate both of these interferences.

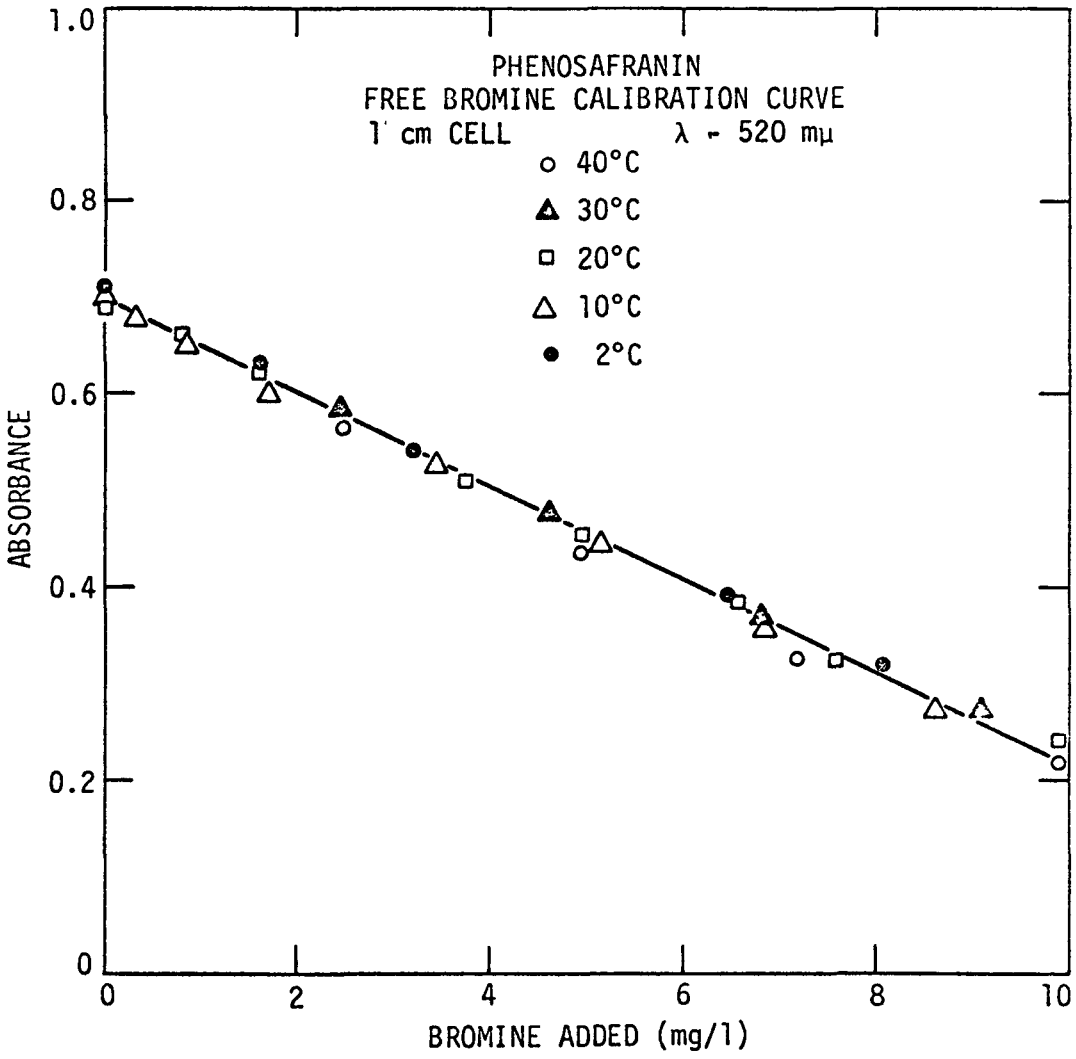
PHENOSAFRANIN
FREE BROMINE CALIBRATION CURVE
1" cm CELL
λ - 520 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
BROMINE ADDED (mg/l)

Figure 5

Reagents;

(1) 0.01% phenosafranin
The phenosafranin reagent solution is stable only for 1 month.

(2) Buffer, pH 9.2 - 0.042 M borax

(3) 1.0% sodium arsenite

Procedure;

To determine free bromine, a 50 ml sample is added with mixing to 3 ml of 0.01% phenosafranin and 5 ml buffer. After 15 seconds, 1 ml 1% sodium arsenite is added. Absorbance is determined within 1 minute at 520 my, pH 9.2.

5. N,N-diethy1-p-phenylene diamine oxalate (DPP oxalate)

Two procedures were evaluated: a colorimetric procedure as used in this laboratory for chlorine determination[1] and Palin's ferrous ammonium sulfate (FAS) titration procedure[2]. The colorimetric test was judged to be the more accurate procedure. With either test, chloramine interferes to some extent (figure 6). 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.

Both free bromine and bromamine react rapidly with DPD. Free bromine reacts within 1 minute, while about 1.5 minutes should be allowed to insure complete bromamine reaction. Chlorine and bromine concentration may be evaluated separately by the addition of ammonium sulfate to the sample to form halogen amines 1 minute before addition of the samples to the reagent. Deleting the ammonium sulfate step allows free chlorine, free bromine, and bromamine to be evaluated free of chloramine; and addition of potassium iodide promotes the reaction of chloramine to give total halogen.

1. A. T. Palin, "The Determination of Free and Combined Chlorine In Water by the Use of Diethyl-p-phenylene Diamine," J.AWWA, Vol. 49. pp.873-880 (July 1957).

2. A. T. Palin, "The Determination of Free Residual Bromine in Water," Water and Sewage Works, Vol. 108, p.461 (1961).

In previous work on chlorine it was established that Mn^{+3} interferes with the test, but that Fe^{+3} and NO_2^- do not[3]. An arsenite modification should be used to eliminate Mn^{+3} interference (0.25 ml 1% sodium arsenite per 100 ml sample).

The reagent as used for chlorine is not temperature dependent, and it is assumed that the same would be true for the bromine test. The free bromine calibration curve (figure 7) is linear from 0.0 to 2.5 mg/1 Br_2 but with an appropriate calibration the range may be extended to 8 mg/1 .

Reagents I

Colorimetric test -

(1) OPD oxalate indicator solution: 1 g DPD oxalate is dissolved in double distilled water containing 8 ml 1+3 sulfuric acid and 0.2 m disodium ethy1enediamine tetra-acetate dihydrate (EDTA). This is diluted to 1 liter, stored in an amber glass-stoppered bottle. The reagent, if stored in a refrigerator, can be used for one month.

(2) Buffer (pH 6.5) - 24 g dibasic sodium phosphate and 46 g monobasic potassium phosphate are dissolved in double distilled water. This solution is combined with 100 ml d.d. water in which 0.8 g EDTA has been dissolved, and then diluted to 1 liter and 20 mg mercuric chloride added .

(3) 1.0% sodium arsenite

(4) Ammonium sulfate (analytical reagent)

Procedure I

Colorimetric test -

(a) To determine tota1 bromine, 50 mg ammonium sulfate is added to 100 ml of sample, mixed, and allowed to stand for 1 minute. This solution is then added to a mixture of 5 ml DPD indicator and 5 ml buffer and mixed thoroughly. The absorbance is determined in 1.5 minutes at 552 my, pH 6.2.

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3. 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.

(b) To determine free chlorine plus totalbromine , 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 in 1.5 minutes at 552 mμ, pH 6.2

(c) To determine total halogen (total bromine + total chlorine), 100 ml of sample is added to a mixture of 5 ml DPD indicator and 5 ml buffer. Then 1 gram potassium iodide is added, and the absorbance is determined in 5 minutes at 552 my, pH 6.2.

Reagents II

FAS titration:

(1) DPD indicator solution as in colorimetric test
(2) Buffer (pH 6.5) as in colorimetric test
(3) Standard ferrous ammonium sulfate titrant - 1.106 g ferrous ammonium sulfate (Mohr's salt) is dissolved in double distilled water containing 1 ml 1+3 sulfuric acid and diluted to 1 liter with freshly boiled and cooled distilled water. The reagent is standardized against 0.0025N standard potassium dichromate.
(4) Potassium iodide (analytical reagent)
(5) Ammonium sulfate (analytical reagent)
(6) Ferroin indicator - 1.485 g o-phenanthroline monohydrate and 0.695 g ferrous sulfate is dissolved in double distilled water and diluted to 100 ml.

Procedure II

FAS titration:

(a) To determine total bromine, 50 mg ammonium sulfate is added to 100 ml of sample, mixed, and allowed to stand for 1 minute. Then the sample is added to a mixture of 5 ml DPD indicator and 5 ml buffer and titrated with FAS to a colorless solution.

(b) To determine total bromine + free chlorine, 100 ml of sample is added to a mixture of 5 ml DPD indicator and 5 ml buffer, and then titrated with FAS to a colorless solution.

(c) To determine total halogen (total bromine + total chlorine), 100 ml of sample is added to a mixture of 5 ml DPD indicator and 5 ml buffer. Then 1 gram potassium iodide is added and after 2 minutes the sample is titrated with FAS to a colorless solution.

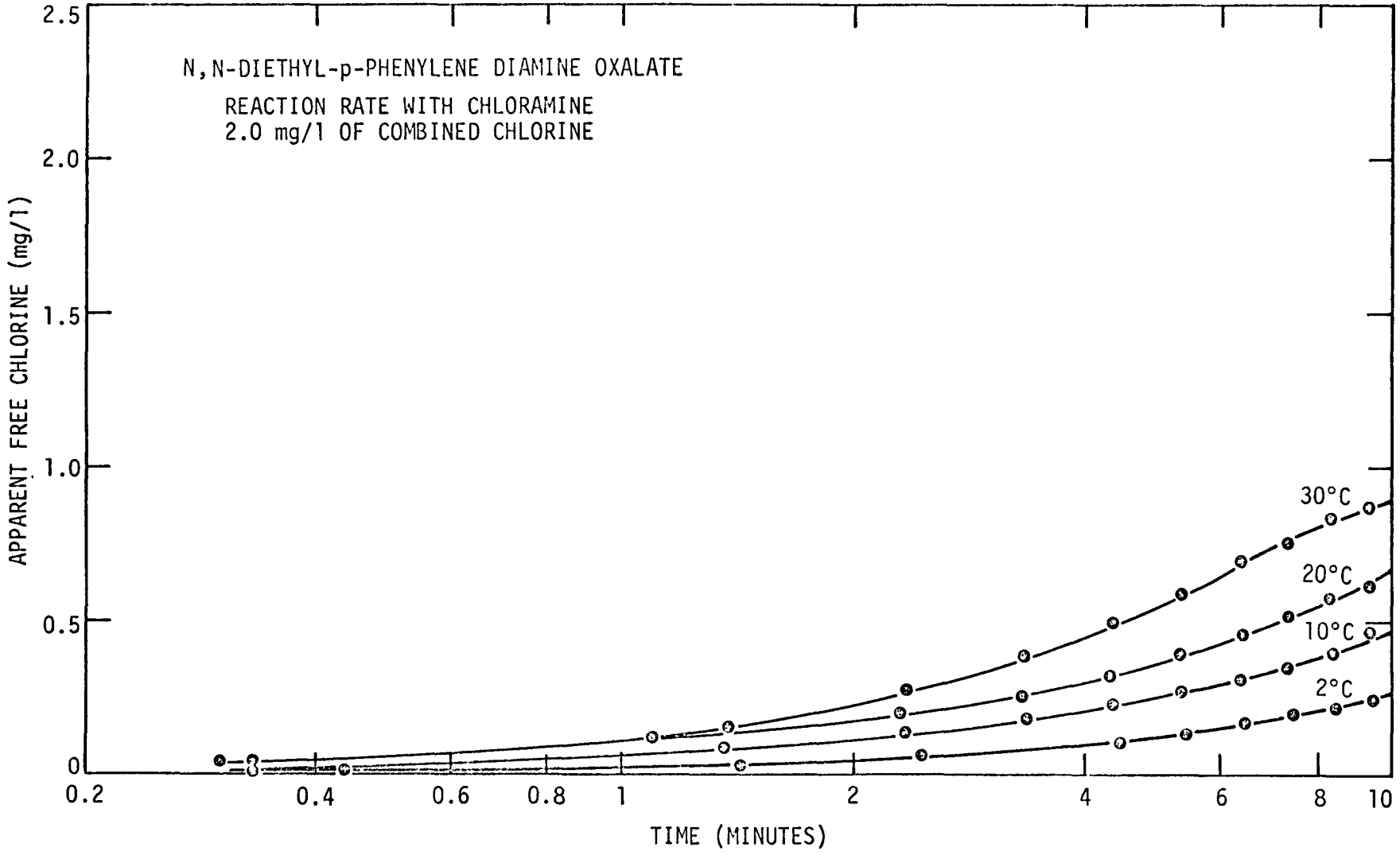
N,N-DIETHYL-p-PHENYLENE DIAMINE OXALATE
REACTION RATE WITH CHLORAMINE
2.0 mg/l OF COMBINED CHLORINE
APPARENT FREE CHLORINE (mg/l)
2.5
2.0
1.5
1.0
0.5
0
0.2
0.4
0.6
0.8
1
2
4
6
8
10
TIME (MINUTES)
30°C
20°C
10°C
2°C

Figure 6

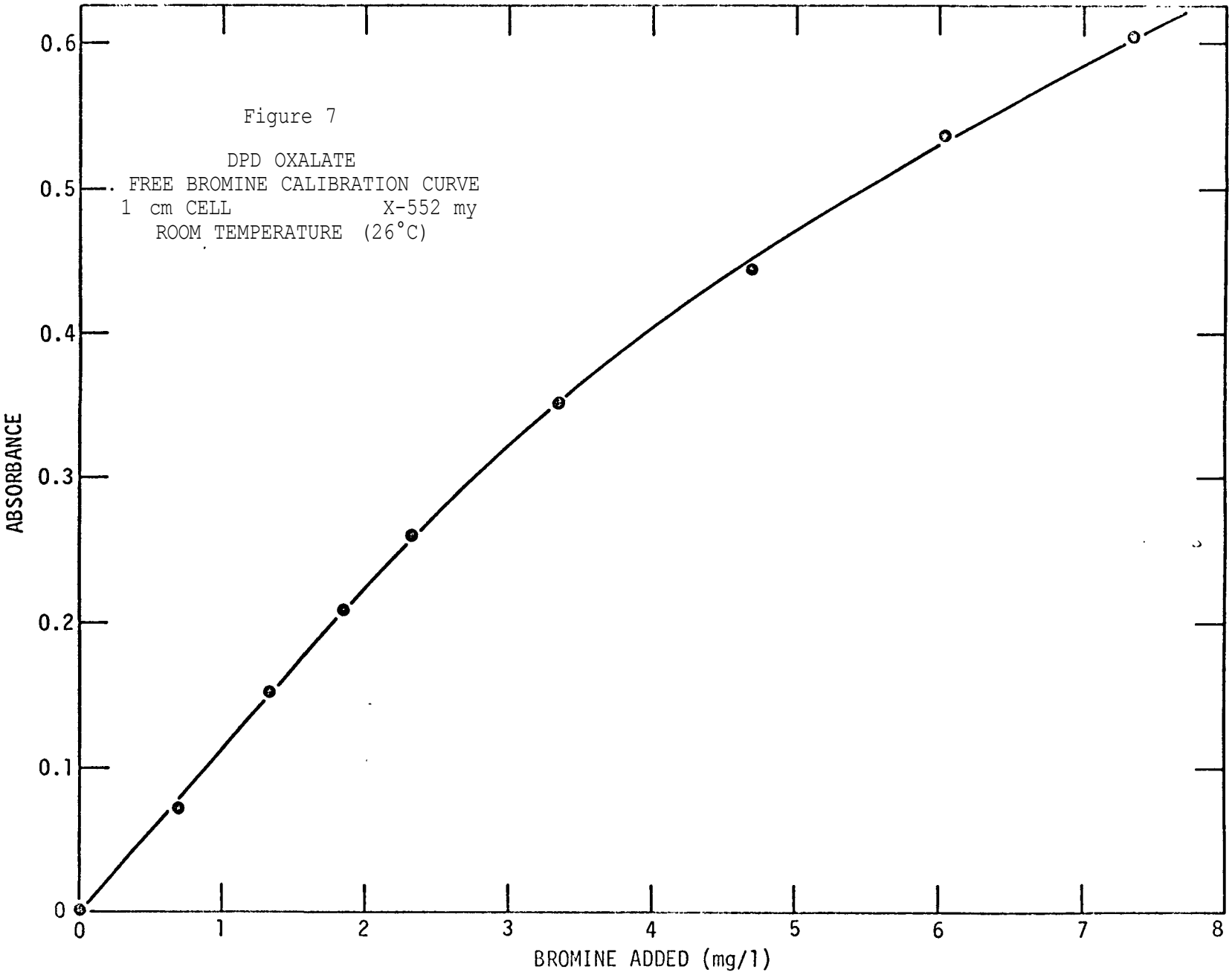
Figure 7
DPD OXALATE
FREE BROMINE CALIBRATION CURVE
1 cm CELL X-552 my
ROOM TEMPERATURE (26°C)
ABSORBANCE
0
0.1
0.2
0.3
0.4
0.5
0.6
0
1
2
3
4
5
6
7
8
BROMINE ADDED (mg/l)

C. THE BREAKPOINT REACTION FOR FREE CHLORINE AND FOR FREE BROMINE

Curves showing chlorine and bromine breakpoint phenomena for water with an ammonia-nitrogen concentration of 1 mg/1 and reaction time of one hour have been prepared at pH 5.0, 7.2, 8.4, and 9.1 (figures 8 to 11).

On a molar basis, the ammonia-bromine reaction appears to be similar to the ammonia-chlorine reaction. The bromamine breakpoint requires 14.1 mg/1 of free bromine, while the chloramine breakpoint requires 6.3 mg/1 of free chlorine.

As reported in our Progress Report of August 1967 and as can be observed in figures 8 to 11 of this report, amine stability is better for chlorine than for bromine.

Methly orange, neutral orthoto1idine , and DPD were the tests used in preparing the ch1orine breakpoint curves as shown in figures 8 and 9. Each of these tests was used to determine both free and total chlorine. Agreement among the tests for the determination of free chlorine was poorest at pH 9.1. Neutral orthoto1idine and DPD values are considerably higher than methyl orange values for free chlorine. Repeated work at this pH gave the same results. It appears that free chlorine and chloramine coexist for a longer time at pH 9.1, and the breakpoint is not distinct under these conditions. The lower pH of the test conditions for the MO determination promotes excessive reaction between the free and combined chlorine.

Brom cresol purple, phenosafran in, phenol red, methyl orange, and DPD were the tests used for preparing the bromine breakpoint curves. BCP and phenosafranin were used to determine free bromine; PR, MO, and DPD were used for the determination of total bromine (figures 10 and 11).

Samples were prepared by the addition of the desired concentration of free Br_2 or $C1_2$ to a buffered solution containing 1 mg/1 NH3 while mixing with a magnetic stirrer.

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4. J. Donald Johnson. "Development of Field Test for Free Chlorine," Annual Progress Report to the Commission on Environmental Hygiene of the Armed Forces Epidemiological Board, Contract No. DA-49193-MD-2442, 1 March 1966 to 30 June 1967.

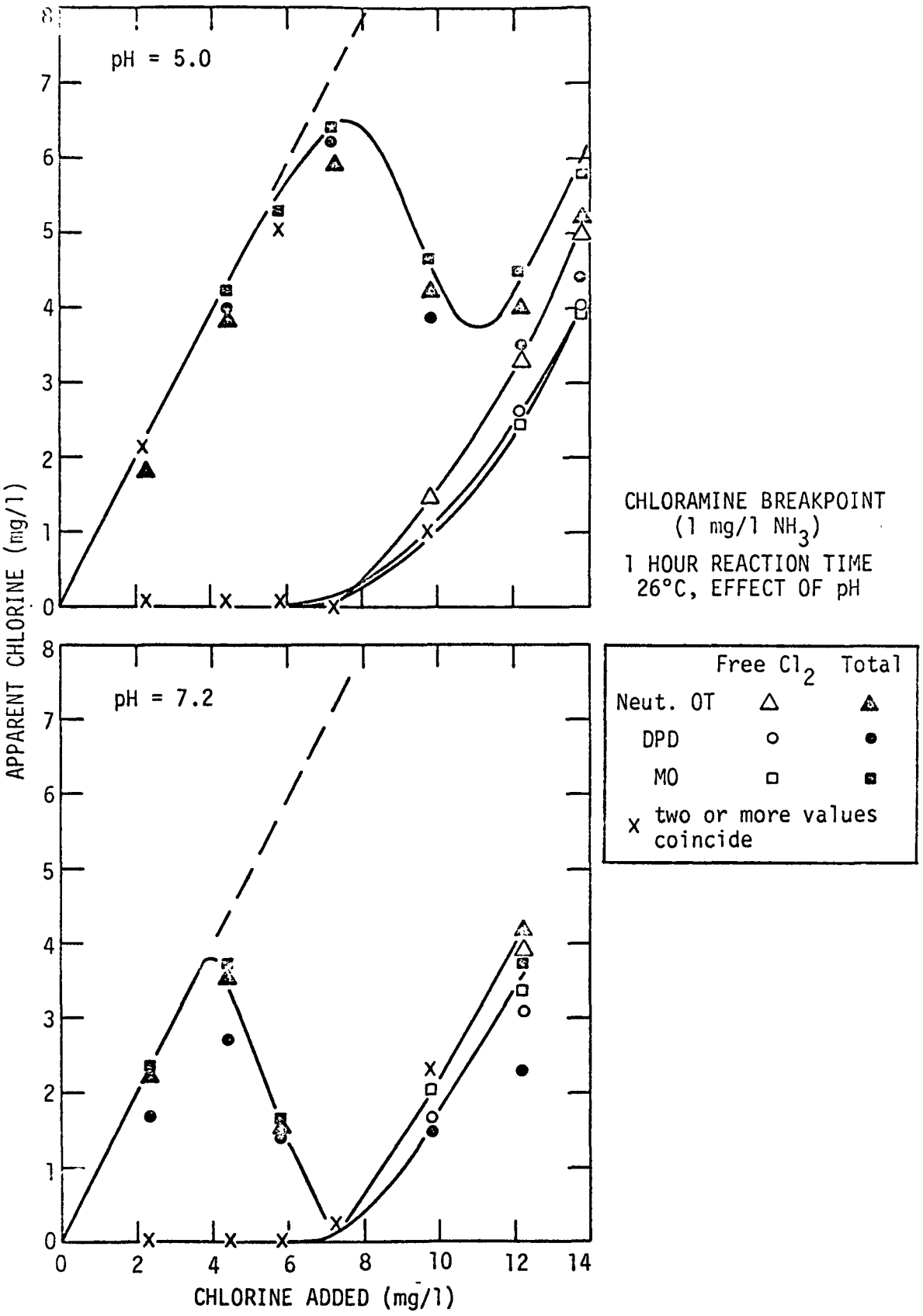

pH = 5.0
pH = 7.2
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
CHLORAMINE BREAKPOINT
(1 mg/l NH3)
1 HOUR REACTION TIME
26°C, EFFECT OF pH
Free Cl2
Total
Neut. OT
DPD
MO
x two or more values coincide

Figure 8

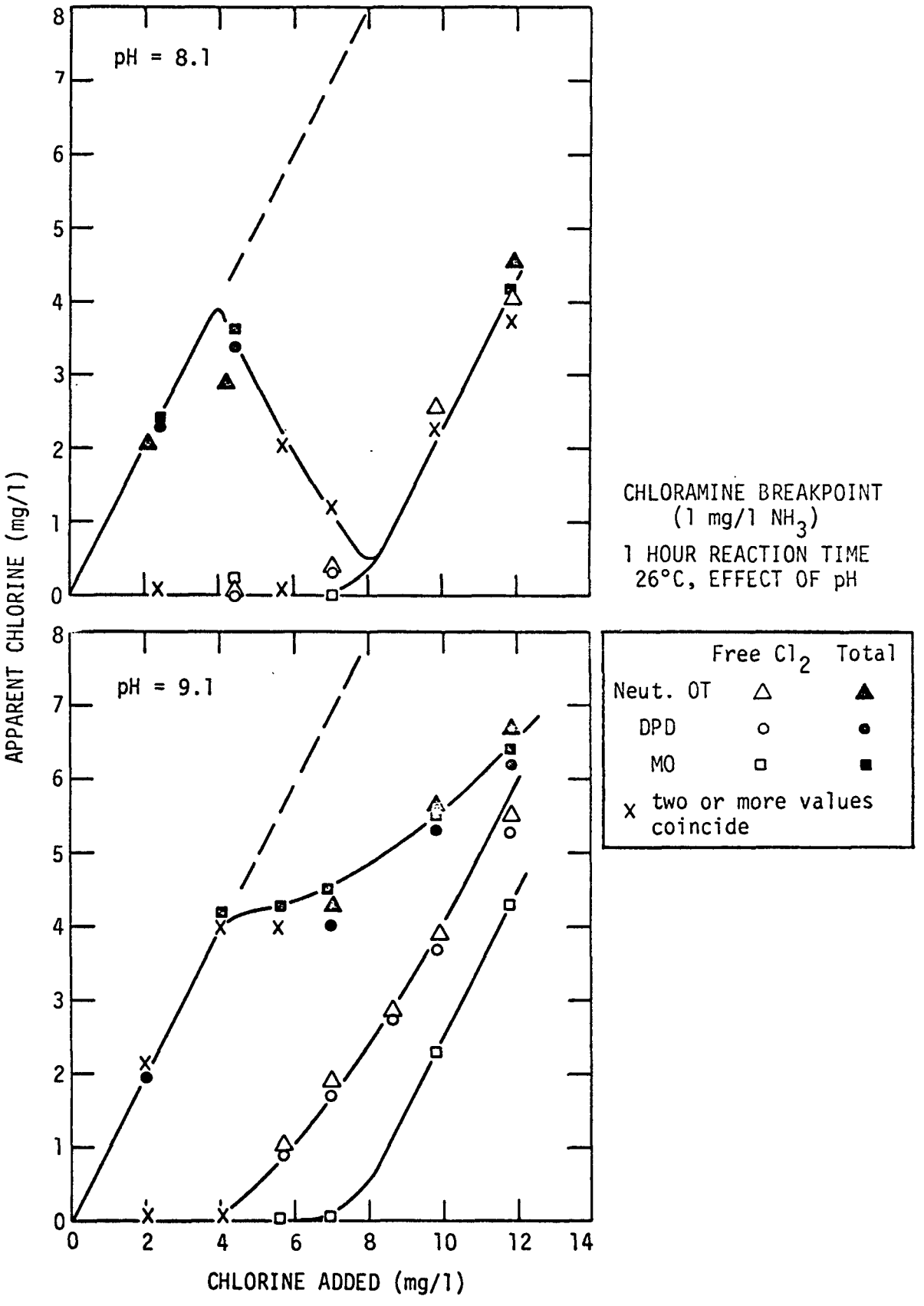

pH = 8.1
pH = 9.1
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
CHLORAMINE BREAKPOINT
(1 mg/l NH3)
1 HOUR REACTION TIME
26°C, EFFECT OF pH
Free Cl2
Total
Neut. OT
DPD
MO
x two or more values coincide

Figure 9

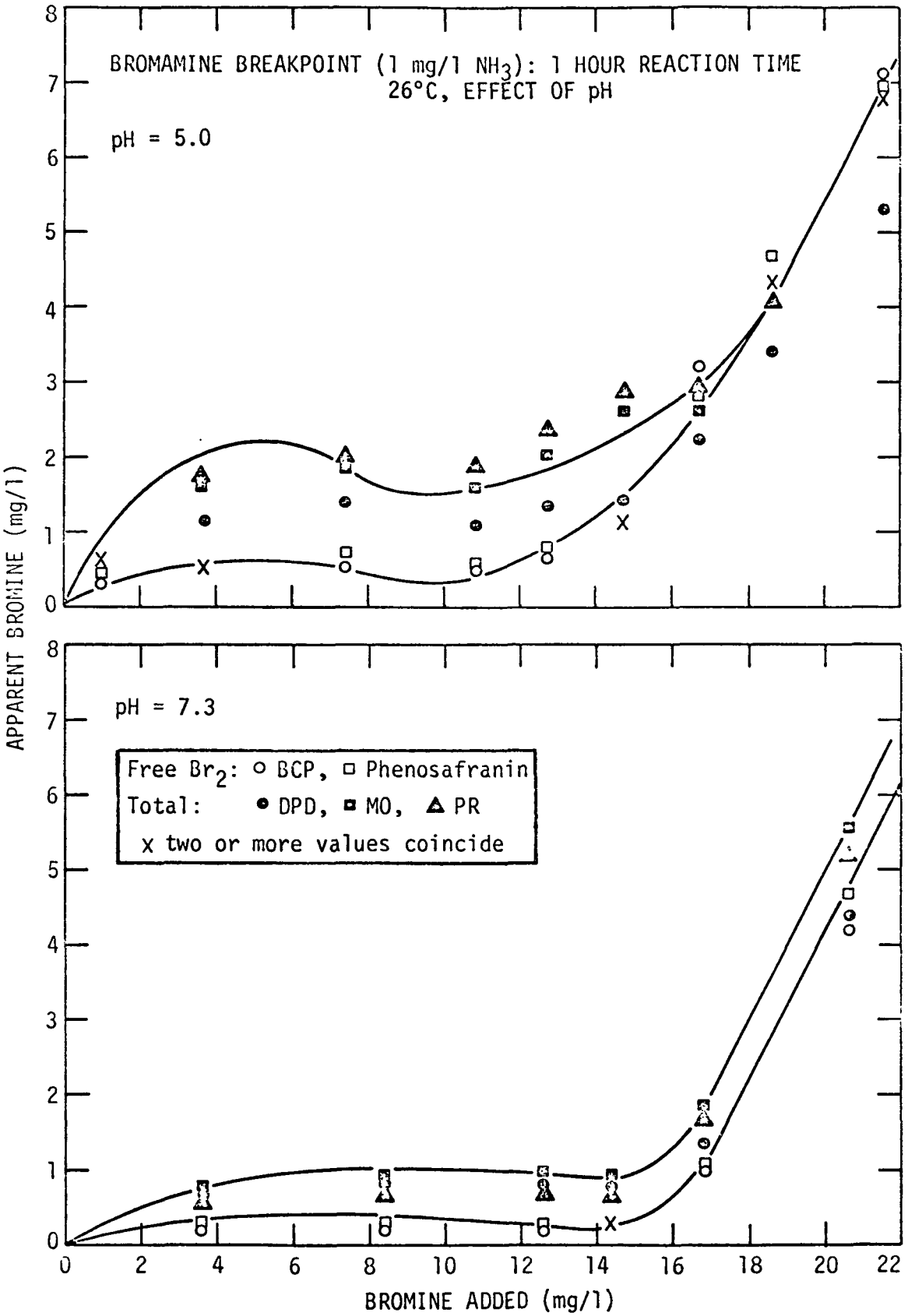

BROMAMINE BREAKPOINT (1 mg/l NH_3): 1 HOUR REACTION TIME
26°C, EFFECT OF pH
pH = 5.0
pH = 7.3
Free Br_2: ○ BCP, □ Phenosafranin
Total: ● DPD, ■ MO, ▲ PR
x two or more values coincide
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
16
18
20
22

Figure 10

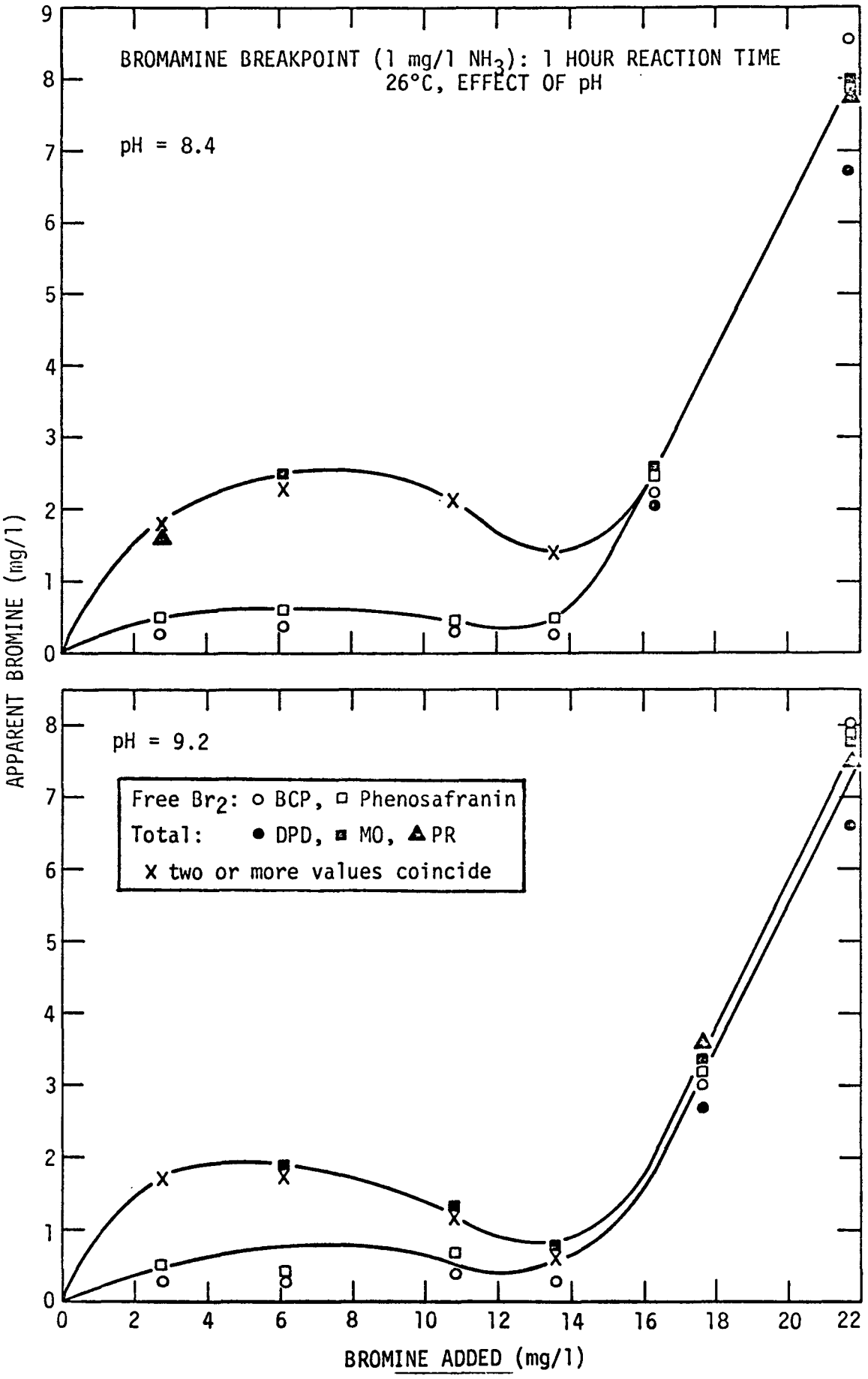

BROMAMINE BREAKPOINT (1 mg/l NH_3): 1 HOUR REACTION TIME
26°C, EFFECT OF pH
pH = 8.4
pH = 9.2
Free Br_2: ○ BCP, □ Phenosafranin
Total: ● DPD, ■ MO, ▲ PR
X two or more values coincide
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
16
18
20
22

Figure 11

The samples were stored in glass-stoppered bottles and aliquots extracted after one hour for testing. Tests were performed as nearly simultaneously as possible, but there was a time lapse of from 3 to 5 minutes from the addition of the sample for the first test to the addition of the sample for the fifth test. This may account for some variation in results with different tests.

D. STUDIES OF BROMAMINE STABILITY

A series of stability tests was carried out at room temperature with 1000 mg/1 NH_3 + 50 mg/1 Br_2 and at pH values of 5.95, 7.1, 7.8, and 8.8 (figure 12). Since the DPD oxalate test is once again being considered for total bromine determination, the sole purpose of this series of bromamine stability work was to make a comparison of the methyl orange test results with the DPD test results. The two tests were in good agreement in the determination of total bromine.

The test procedure was as follows: Free bromine (as NaOBr) was added to a buffered solution containing 1000 mg/1 ammonia. During bromine addition, samples were mixed by means of a magnetic stirrer to insure complete mixing and to eliminate the possibility of error due to local excesses of bromine or ammonia. At specified time intervals, samples were withdrawn and analyzed for total bromine using the DPD and the methyl orange procedures.

E. THE REACTION OF CHLORINE WITH BUFFERED SOLUTIONS CONTAINING AMMONIA AND BROMIDE ION

A study was made of the chemistry of the reactions of chlorine when added to solutions containing ammonia and bromide ion and at varying pH (figure 13).

1.85 mg/1 free chlorine was added to previously buffered samples containing 1 mg/1 ammonia (from ammonium chloride) and bromide ion (from sodium bromide). The bromide ion concentrations were 1, 3, 5, 25, 100, and 250 mg/1. The range of pH values was from 5 to 9. The total bromine concentrations were determined after 10 minutes contact time by the phenol red test. The phenol red test was used because it is completely insensitive to chlorine and chloramines. Ultra violet absorption was used to determine the species of halogen-amine that was formed.

An examination of figure 13 shows that bromamine formation is dependent upon pH and bromide ion concentration. At pH 7 or above, no detectable quantity of bromamine is formed unless the bromide ion concentration exceeds 5 mg/1.

Total available halogen was also determined with methyl orange. With the higher bromide concentrations, methyl orange values were lower than the phenol red results, due to decomposition of a portion of the bromamines at the low pH required in the methyl orange test.

EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE (26°C)

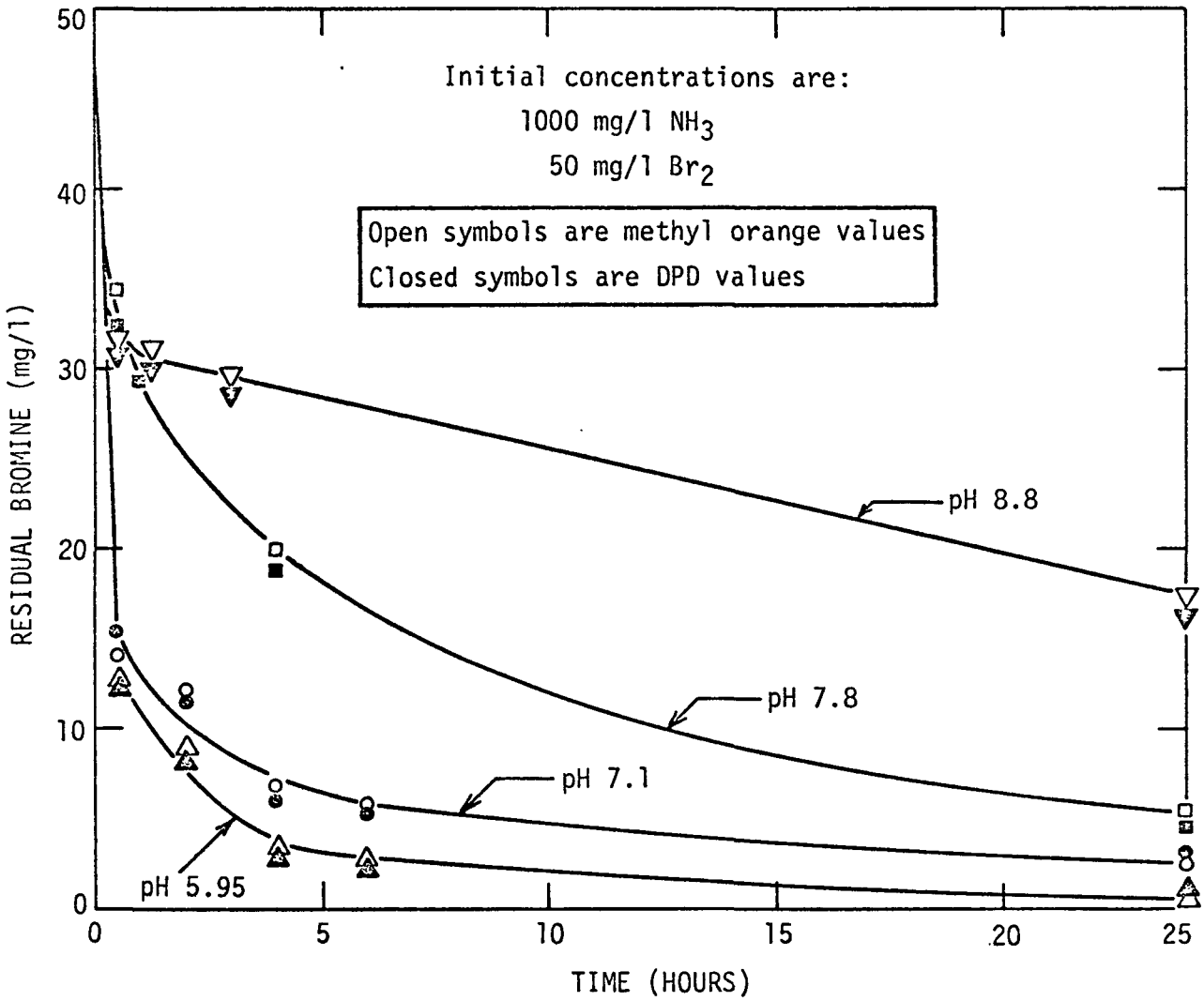
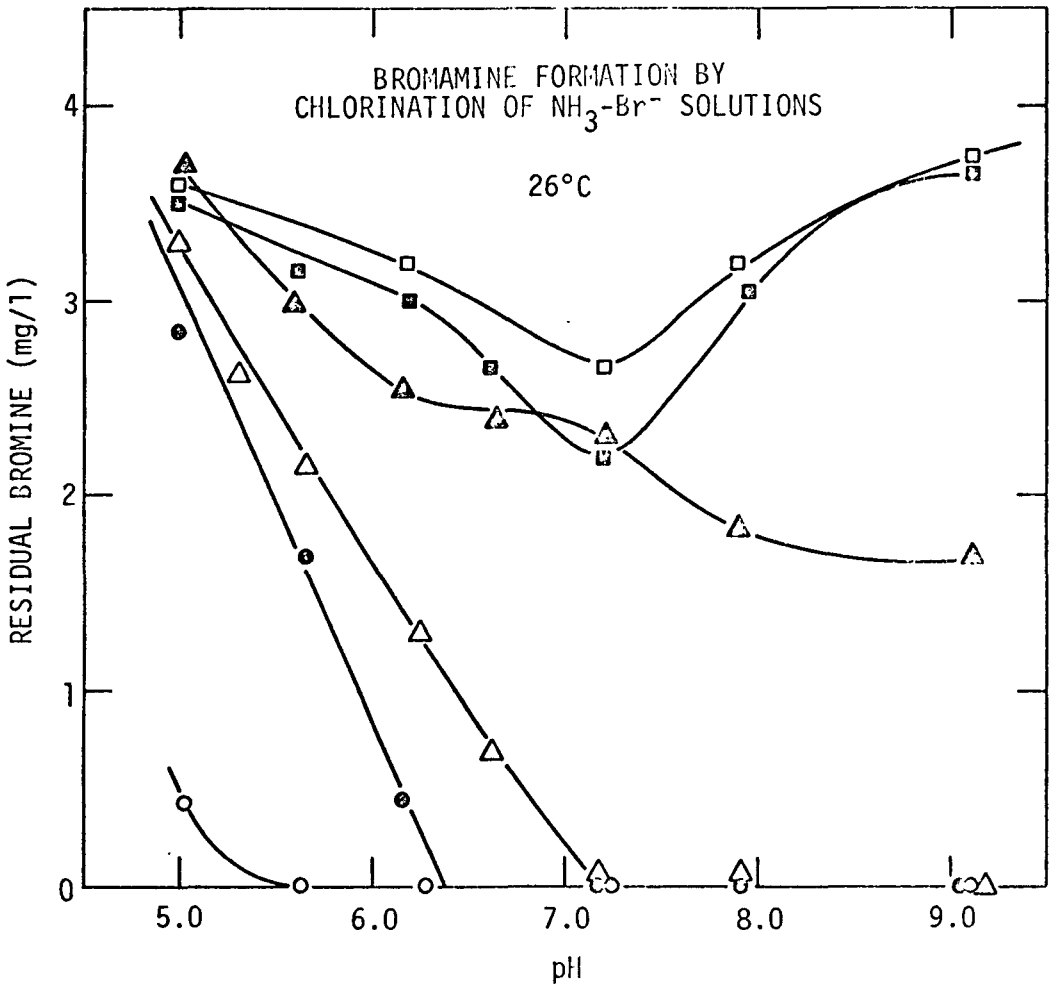


Figure 12



Initial conditions:

1 mg/l NH_3 (from NH_4Cl)

1.85 mg/l Cl_2 ($\rightleftharpoons$ 4.16 mg/l as Br_2)

○	1 mg/l Br^-
◐	3 mg/l Br^-
△	5 mg/l Br^-
◬	25 mg/l Br^-
□	100 mg/l Br^-
◨	250 mg/l Br^-

Residual Bromine was determined by Phenol Red test after 10 min. contact time

Figure 13

In the presence of 25 mg/1 of bromide ion or more, the formation of some bromamine occurs over the entire pH range tested. Therefore, it appears that a high concentration of bromide ion or low pH is necessary for the bromide ion to be oxidized and subsequently form bromamine.

Ultra violet absorption showed that under the reaction conditions stated in paragraph 2 above, tribromamine is formed at pH values between pH5 and pH6, a mixture of tribromamine and monochloramine is formed at pH values between 6 and 7» and monoch1oramine alone is formed at pH values between pH7 and pH9.

Work is in progress to determine the effect of varying concentrations of ammonia on this reaction.

F. BROMINE DEMAND OF AMMONIA AND AMINO ACIDS

The four colorimetric procedures for the determination of free and combined bromine were evaluated for their performance in water containing ammonia and amino acids. The tests under study are brom cresol purple and phenosafranin for free bromine and methyl orange and phenol red for total available bromine.

Varying concentrations of bromine were added to ammonia or amino acid samples and after the desired contact times free and total residual bromine were determined by the proper tests.

The water used for these tests was free of ammonia and contained 150 mg/1 each of alkalinity and hardness. The pH was adjusted with carbon dioxide.

Solutions of ammonium chloride, glycine, and L-cystine were prepared in ammonia-free water containing 150 mg per liter each of alkalinity and hardness (prepared as described above) and adjusted to pH 6, 7, or 8. For each sample the nitrogen (N) concentration was 0.3 mg/1. The temperature of the samples and the tests was 26 C (room temperature). The contact times were 1 hr., 4 hrs., and *2k* hrs.

The ammonium chloride samples were prepared only at pH 7 (figure 14*)*. The breakpoint for these samples occurred at a free bromine dosage of 6.2 mg/1 (as Br_2). Brom cresol purple and phenosafranin were in good agreement for free residual bromine as were the methyl orange and phenol red values for tota1 residual bromine.

BROMINE DEMAND - AMMONIUM CHLORIDE (0.3 mg/1 N) : pH 7.3-8, 26°C
150 mg/1 each ALKALINITY AND HARDNESS

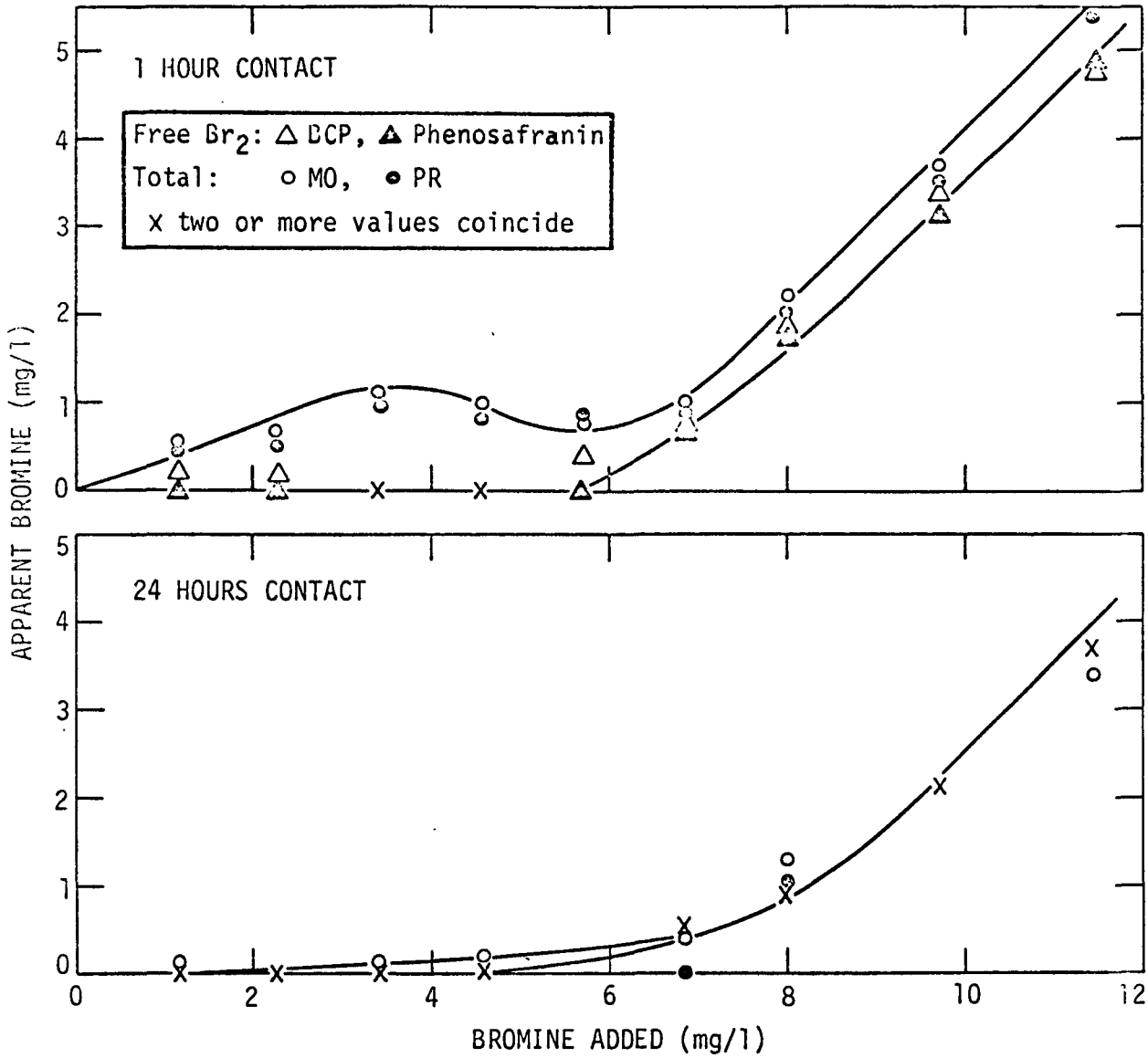


Figure 14

BROMINE DEMAND - GLYCINE (0.3 mg/1 N) : pH 6-6.7, 26°C,
150 mg/1 each ALKALINITY AND HARDNESS

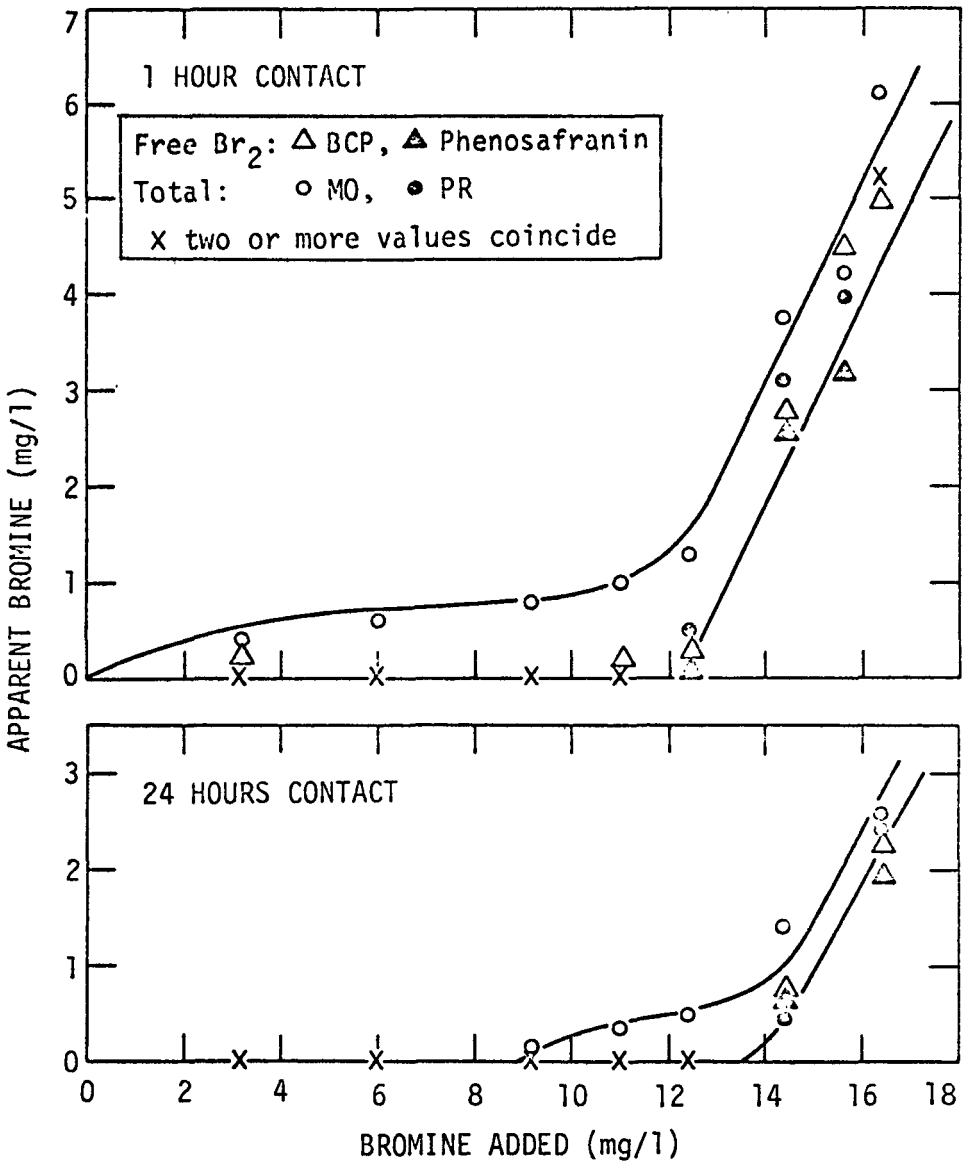


Figure 15

BROMINE DEMAND - GLYCINE (0.3 mg/1 N): pH 8-8.5, 26°C
150 mg/1 each ALKALINITY AND HARDNESS

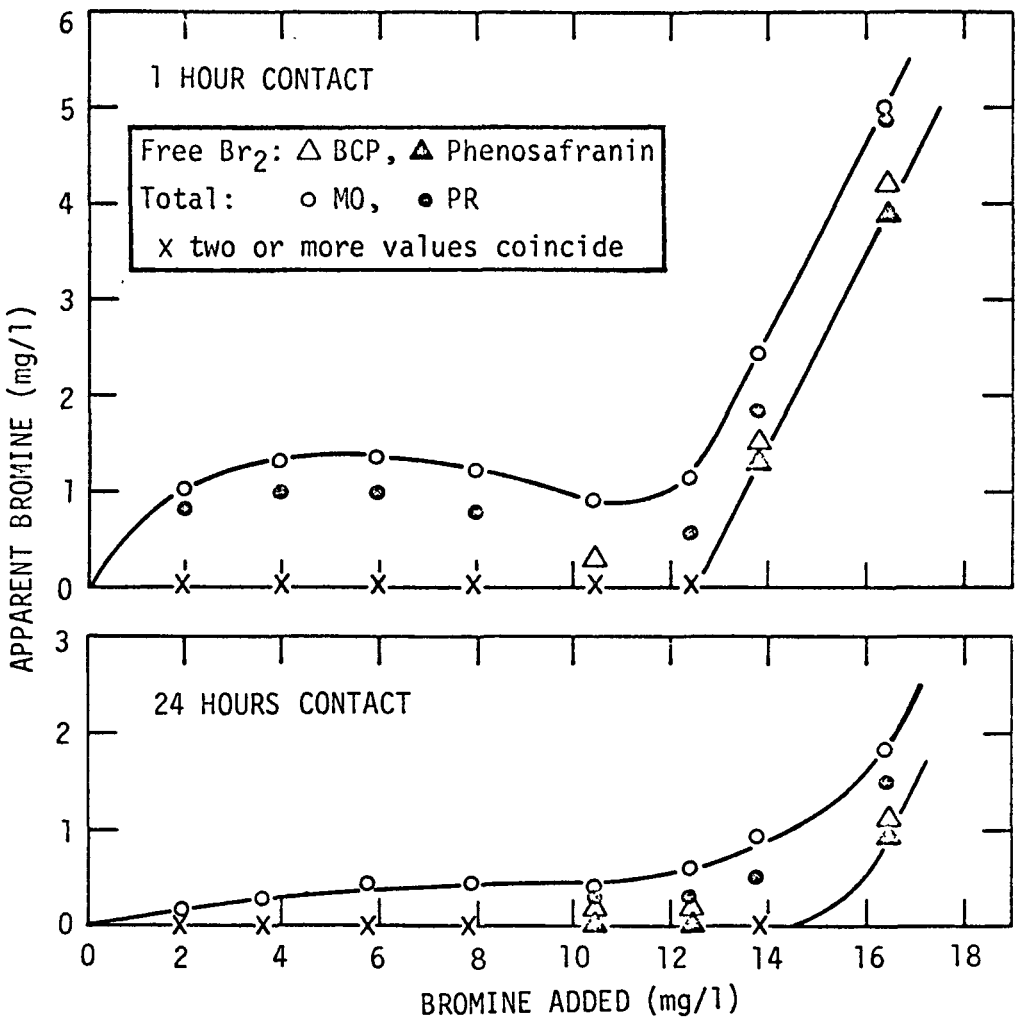


Figure 16

BROMINE DEMAND - L-CYSTINE (0.3 mg/1 N): pH 5.9-6.4, 26°C
150 mg/1 each ALKALINITY AND HARDNESS

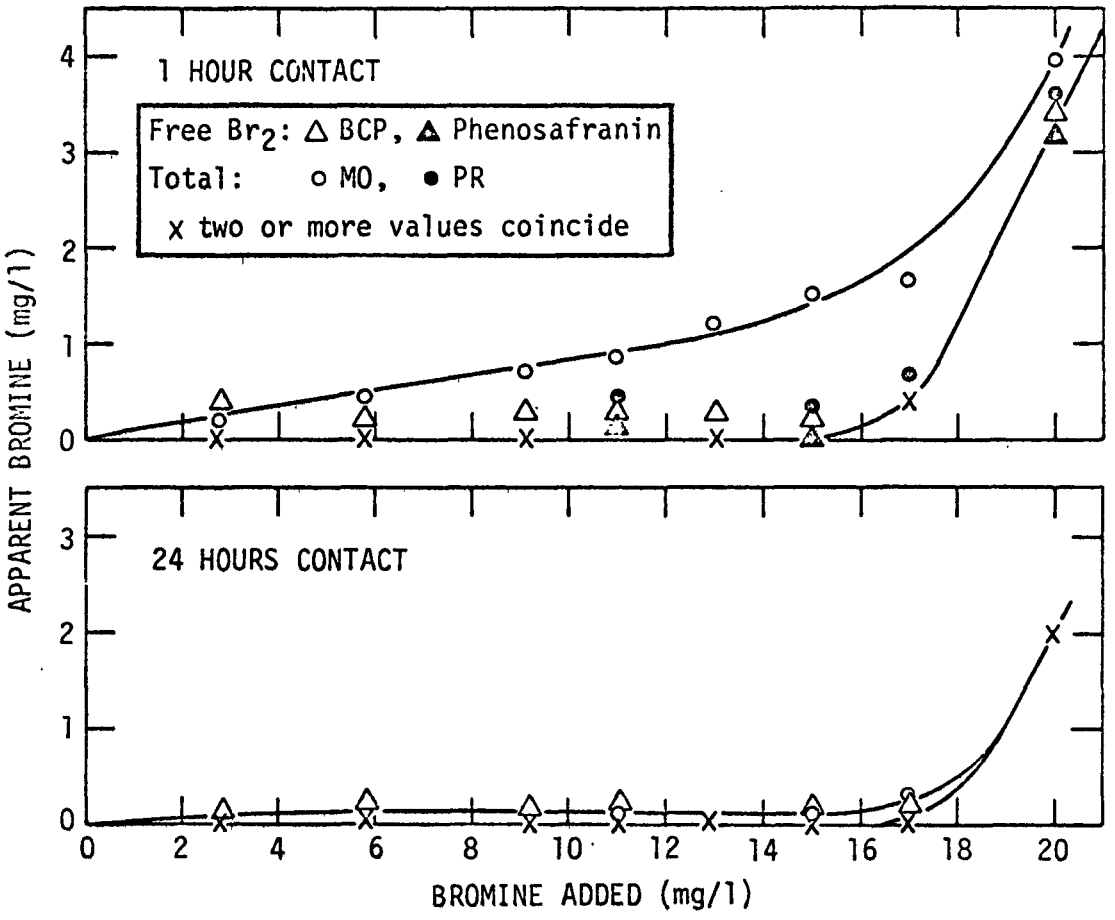


Figure 17

BROMINE DEMAND - L-CYSTINE (0.3 mg/1 N); pH 7.7-8.4, 26°C
150 mg/1 each ALKALINITY AND HARDNESS

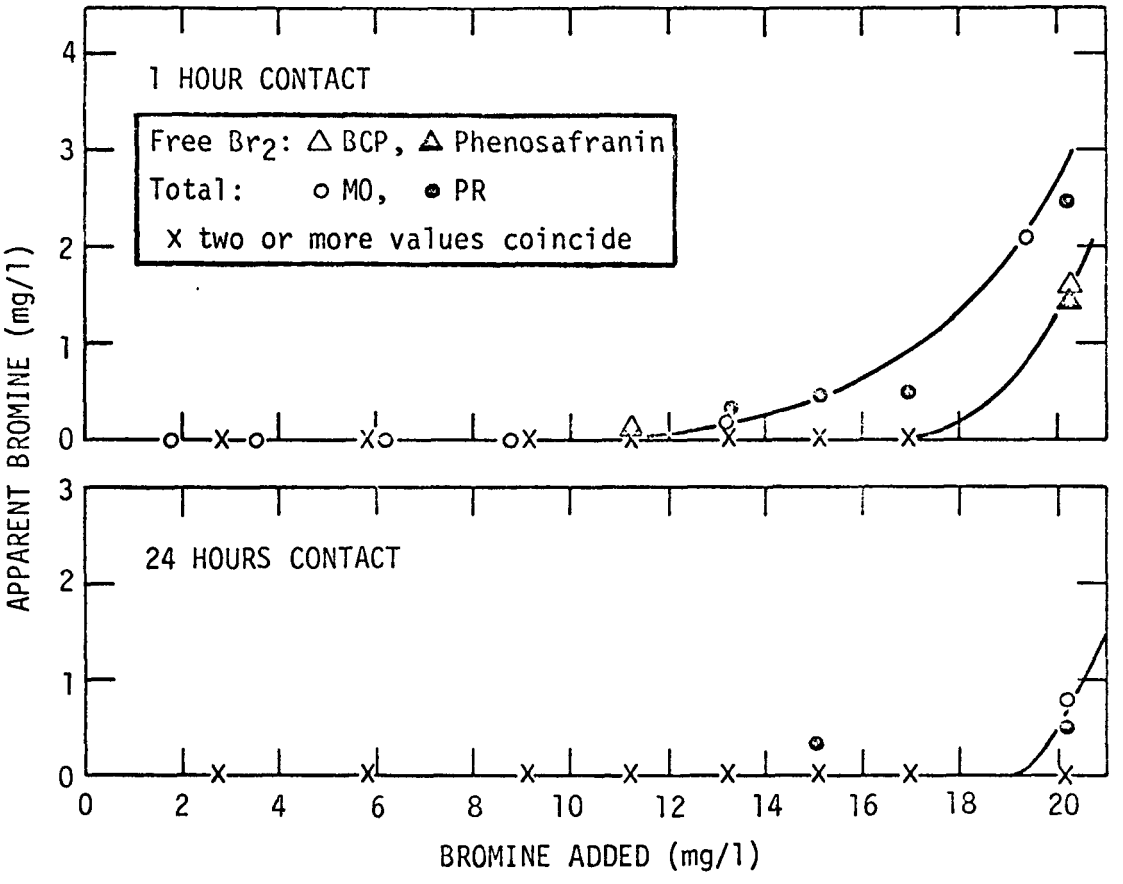


Figure 18

G1ycine-bromine samples were prepared at pH values of 6.5 and 8, (figures 15 and 16). The glycine concentration was equivalent to 0.3 mg/1 of nitrogen. Samples at both pH values showed a breakpoint at a dosage of about 12 mg/1 free bromine. Prior to the breakpoint, the methyl orange values were higher than the phenol red values for total residual bromine.

L-cystine was treated with bromine at pH values of 6 and 8, (figures 17 and 18). Methyl orange values were considerably higher than phenol red values for total bromine. Such apparent differences in results for total bromine are probably due to the non-linearity of the phenol red calibration curve with low Br_2 concentrations.

The brom cresol purple and the phenol red tests were modified slightly in order to improve results. For the brom cresol purple test, the pH was raised from 9 to 9.30 by using 10 ml pH 9.4 borate-sodiurm hydroxide buffer. In order to determine the very low total bromine residuals more accurately (0-0.7 mg/1 Br_2) a phenol red reagent solution of 0.001% strength was used.

In general the values for free bromine determined by BCP (pH 9.3) and phenosafranin (pH 9.1) were in good agreement. The methyl orange test (pH 2) showed higher total residual bromine values prior to the breakpoint than did the phenol red test (pH 5.1).

Another project in this laboratory deals with the disinfection of sewage effluents. In this work, it was found that the amperometric titration and the DPD test gave results which were in good agreement, whereas the orthotolidine and methyl orange procedures gave much lower results. Presumably, this is due to a rapid reaction of the chloramines with reducing substances in the effluents at the low pH (1 and 2) required for the tests.

It is assumed that a similar effect would be observed with bromine, and tests are planned to verify this.

G. SUMMARY OF RESULTS

Since the last Annual Progress Report, the four colorimetric tests recommended for the determination of free bromine and bromamine , brom cresol purple, phenosafranin, methyl orange, and phenol red, have been further evaluated. More recent work has included Palin's DPD oxalate test for total "residual" bromine. Minor changes in reagent concentration and buffer strength for PR and BCP

have become necessary as work has progressed. The reagents have been tested for stability which appears to be one month for PR, BCP, phenosafranin and DPD. MO is stable for at least three months.

The reactions of free chlorine in buffered solutions containing 1 mg/1 ammonia nitrogen and varying concentrations of bromide ion have been studied in greater detail. Results indicate that high concentrations of bromide ion or low pH are necessary for formation of bromamines.

Some bromamine stability studies for one hour contact times were repeated for the purpose of comparing MO and DPD test results. The results are in good agreement.

An evaluation of four colorimetric tests, brom cresol purple, phenosafranin, methyl orange, and phenol red is being made in water containing ammonia and amino acids. Brom cresol purple and phenosafranin show good agreement in the determination of free bromine, while methyl orange and phenol red are in fairly good agreement in the determination of total bromine. This work is a preliminary to an evaluation of the performance of these tests in polluted water. To such an evaluation will be added a fifth test, DPD, for total bromine. The DPD test will be used since other work in this laboratory has shown that at the low pH required by the MO test there may be a rapid reaction of the chloramines (and possibly the bromamines, though this has not yet been tested) with reducing substances in the sample.

H. CONCLUSIONS

The brom cresol purple and phenosafranin tests are suitable for the determination of free bromine. The DPD oxalate, methyl orange, and phenol red tests are suitable for the determination of total bromine.

Studies of the bromine demand of solutions of ammonia and amino acids indicate good agreement in results among the tests for free bromine and bromamine.

Studies to date of the reaction of chlorine with solutions containing bromide ion and ammonia indicate that in order to form bromamines in a water supply by addition of chlorine and bromide ion, these would have to be added to a small volume at low pH for bromine formation with subsequent mixing of this solution with the remainder of the water to be treated.

Future work will include a more thorough evaluation of the DPD oxalate test for the determination of total bromine. The effect of temperature and interfering substances will be determined.

The DPD test as well as the brom cresol purple, phenosafranin, methyl orange, and phenol red tests will be evaluated for their performance in highly polluted water.

Future work will include a more detailed study of the reaction of chlorine with solutions containing ammonia and bromide ion, and in particular, the effect of varying concentrations of ammonia in such solutions.

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security claasification of (title, *body* of absfract *and Indenting* annotation must be entered when the overall report *la classified)*

1 ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
ILLINOIS STATE WATER SURVEY Urbana, Illionis	2b OROUP

3 REPORT TITLE

DETERMINATION OF FREE BROMINE IN WATER

4 DESCRIPTIVE NOTES (Typo of report and *incluaive dates)*

Annual Progress Report 1 July 1967 to 30 June 1968

5 AUTHOR(S) (Last *name. first* name, Initial)

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

6 REPORT DATE	7a. TOTAL NO OF PACES	7b. NO. OP REPS
August 1968	38	

8a CONTRACT OR ORANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA-49-193-MD-2909 b. PROJECT NO.	2
c. d	9b. OTHER REPORT NO(S) *(Any* other numbers that may be resigned *this* report)

10 AVAIL ABILITY/LIMITATION NOTICES

Qualified requesters may obtain copies of this report from DDC.

11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U. S. Army Medical Research and Development Command, Washington, D.C.

13 ABSTRACT 20315

The four selected colorimetric reagents, methyl orange, phenol red, brom cresol purple, and phenosafranin, have been evaluated in waters containing ammonia and amino acids. In general, brom cresol purple and phenosafranin were in good agreement for the free bromine determinations, and methyl orange and phenol red were in fairly good agreement for the total residual bromine determinations.

In a study of the disinfection of activated sludge effluents, it was found that both acid ortho-tolidine and methyl orange produced low results in the determination of total available chlorine, whereas DPD gave values in better agreement with amperometric titration values. It appears probable that this effect will also be found with bromine in highly polluted waters, and for this reason DPD will be included in future evaluations.

Studies made on the stability of the phenol red, brom cresol purple, and phenosafranin reagent solutions indicate that the three reagents are stable for four weeks but should not be used thereafter.

DD FORM 1 JAN 64 1473

Security Classification

14. KEY WORDS

Analysis
Water
Bromine
Methyl Orange
Phenol Red
Brom Cresol Purple
Phenosafranin
N,N-diethyl-p-phenylene diamine Oxalate

Studies on the chlorination of solutions containing ammonia and bromide ion indicate that bromamine formation is dependent upon pH and bromide concentration and possibly upon ammonia concentration. At pH 7 or above, no detectable quantity of bromamine is formed and no loss of chlorine occurs unless the bromide ion concentration exceeds 5 mg/1.