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DETERMINATION OP FREE BROMINE IN WATER (U)

FINAL REPORT

by

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Determination of Free Bromine in Water

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I. SUMMARY

The major objective of this work has been the development of suitable analytical 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, chloramines, and bromamines. 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.

Bromine-ammonia and chlorine-ammonia breakpoint curves have been determined for varied contact times and at different pH values. The reaction of bromine appears to be more rapid than that of chlorine, especially at high pH.

Studies of the stability under varying ammonia-to-bromine ratios and varying pH values indicate that the bromamines are far less stable than the chloramines.

The six colorimetric reagents listed above have been examined for response to mono-, di-, and tribromamine. To insure a minimum amount of reaction of the bromamines with the BCP, PS, and MO (pH 9.5) reagents, the premixed buffer and sample must be added to these reagents. To obtain a maximum response to the bromamines, specifically NBr_3, potassium iodide must be added to the sample prior to testing with DPD. The response of the MO and PR tests to the bromamines is complete.

Studies made of the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide ion indicate that the reaction to form bromamines depends primarily upon pH.

A number of the selected methods have been evaluated for their performance in water containing ammonia and amino acids. This was a preliminary to a study of their performance in polluted water. In both studies, brom cresol purple and phenosafranin were in reasonably good agreement for the free bromine determinations. In the determination of total available bromine, DPD gave the highest values followed by methyl orange (pH 2) and phenol red. In both studies the breakpoint curves determined by these methods were also compared with similar curves determined by two different amperometric titration procedures.

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47 10 " "

48 5% and 10% Activated Sludge Effluent

49 2% and 10% Primary Effluent

IV. DETERMINATION OF FREE BROMINE IN WATER

A. Introduction

Under certain circumstances neither chlorine nor iodine is entirely satisfactory as a viricidal and germicidal agent in the preparation of potable water. Many water sources contain ammonia in such quantity that chlorination results in the formation of chloramines which are far less effective as disinfectants than free chlorine; and iodine effectiveness decreases with decreasing pH and with increasing concentration of iodide ion. It appeared possible that bromine had properties which would avoid these problems. Although free bromine is usually approximately equivalent on a molar basis to free chlorine in disinfecting ability, the bromamines are reportedly far more effective than chloramines, approaching free bromine and free chlorine in effectiveness. A greater knowledge of the chemistry of bromine and bromamines in dilute solutions was necessary for a thorough evaluation. In order to evaluate the effectiveness of bromine as a disinfectant, analytical methods which could easily be adapted for field use were necessary for determining bromine and the bromamines.

The most comprehensive work on the chemistry of bromine and bromamines is that of Johannesson. He suggests[1] that monobromamine is a more potent bactericide than monochloramine due to the formation of the monobromammonium ion (NH_3Br^+) which dissociates to ammonia (NH3) and a positively charged bromine atom (Br^+) having strong oxidizing powers.

Only one test has been available for distinguishing free and combined bromine. This is the amperometric titration proposed by Johannesson[2]. and is based on the assumption that the free and combined forms do not coexist. Addition of ammonia causes a reduction of the diffusion current if the bromine is present in the free state and no change if it is combined. By the usual titration, the total bromine can be determined. Chlorine and chloramines may be determined in the same way if potassium iodide is added to permit titration of the chloramine, either present originally or formed upon addition of the ammonium salt. (Our experience with Johannesson's amperometric titration showed some loss of halogen, particularly bromine, apparently due to the rapidity of stirring and the length of time required to complete the test).

Johannesson[2] has also used the neutral orthotolidine FAS titration for total bromine and Palim[3] has adapted the DPD procedure for this purpose.

B. Methods Evaluated

In this study twenty-seven reagents have been evaluated for possible use in the determination of free and combined bromine. Bromamines can be formed by the addition of liquid bromine to water containing ammonia or by adding a soluble bromide, followed by chlorine or a hypochlorite. In the latter method, which might be preferred for field use, both chloramines and bromamines are formed. 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. Therefore, the ideal method should permit the determination of free bromine, free chlorine, bromamines, and chloramines, either when present alone or with other members of this group. Distinguishing between free chlorine and free bromine is probably not of the utmost importance, but because of 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 10 C, and interference from inorganic compounds (Fe^{+++}, NO_2^-, and Mn+++).

The reagents which were evaluated earlier for free chlorine tests[4] were included in the group for possible evaluation in the determination of free bromine. Others were chosen from those suggested in the literature and those with low oxidation reduction potential values which might be oxidized by free bromine but not by free chlorine.

Many of these reagents proved to be unsatisfactory and were discarded. These reagents are listed in Table 1 with the reasons for their elimination.

Other reagents, which would be satisfactory except for certain interferences, have been set aside in favor of a few reagents showing greater promise. Those set aside are included in Table 2 which shows free chlorine, chloramine, and bromamine interference.

The five reagents selected as most promising are methyl orange, DPD oxalate, phenol red, brom cresol purple, and phenosafranin. These were selected primarily because interferences due to chloramine, ferric ion, nitrite ion, and manganese are low. 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.

C. Experimental Methods

Bromine demand-free water was used in the preparation of all reagents and samples. To prepare bromine demand-free water, tap water was first deionized and then distilled from acid in all glass apparatus to remove ammonia.

All glassware and other equipment in contact with bromine samples were either soaked in a strong bromine solution or cleaned with chromic acid and rinsed thoroughly with the bromine demand-free water before use.

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 tested.

Amperometric titrations were performed using a Wallace and Tiernan Amperometric Titrator.

A Sargent water bath and cooler was used in controlled temperature studies.

Calibration curves for bromine and chlorine were prepared using a series of dilutions of an iodometrically standardized bromine or hypobromite solution and a sodium hypochlorite solution. (The preparation and standardization procedure for free bromine and free chlorine stock solutions are described in Appendix 1, section VI). For every method the proper portion of these dilutions was simply added to the combined reagent-buffer mixture and the resulting absorbance was plotted against the free halogen concentrations.

For the methyl orange (pH 2), DPD, and phenol red reagents, the tests were performed as for calibration, by adding the sample to a premixed buffer and reagent 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) tests, the premixed buffer and sample were added to the reagent. This order of addition of reagents keeps bromamine interference to a minimum. In the preparation of free bromine calibration curves this order of addition is not important since bromamines should not be present and the sample may be added to the combined reagent-buffer mixture.

D. Methods - Results and Discussion

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 addition of 1 ml of chloroacetic acid (91 g/100 ml) produces the correct pH of 1.8 to 2.1 for samples containing up to 1000 mg/1 of alkalinity.

This test relies on a bleaching reaction, and for this reason, accurate measurement of the reagent is necessary. The sample must be added to the acidified reagent with rapid mixing. It is important that there be an excess of methyl orange reagent at all times. If methyl orange is added to the sample, or if the sample is added without adequate mixing, the bromine in the sample will not bleach the methyl orange quantitatively. When addition of the sample to methyl orange produces a colorless solution, the test must be repeated with a dilute sample or with the larger quantity of methyl orange required.

At the low pH required for the MO test, there are three possible interferences: (1) chloramines, if present in the sample, react slowly with methyl orange; (2) if the sample contains bromide ion, this chloramine interference increases; (3) if the sample 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. To limit these interferences, absorbance should be determined at 1.5 minutes reaction time.

Ferric and nitrite ions do not interfere, and interference due to manganic ion may be reduced by use of an arsenite modification. The rate of reaction of chloramine with methyl orange is shown in Figure 1 and the extent of interference depends upon the time allowed before reading. In the 1.5 minutes necessary for the complete reaction of bromine, there is a negligible chloramine interference. However, the subsequent addition of bromide ion promotes a rapid quantitative reaction of chloramine.

The calibration curves at temperatures of 2 to 40°C are linear and cover the range of 0.0 to 4.0 mg/1 as bromine (Figure 2). The following volumes of standard methyl orange solution generally apply in the indicated bromine range: 5 ml for the range of bromine below 1.9 mg/1, 10 ml for the 1.75-4.0 mg/1 range. The absorbance of methyl orange solutions

is slightly temperature dependent. For greatest accuracy, calibration should be performed at a temperature near that used for the tests.

Reagents:

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

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

(3) Bromide. 2.6% solution of sodium bromide

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

Procedure:

To determine total bromine plus free chlorine, a 50 ml sample is added with mixing to 5 ml 0.005? MO previously mixed with 1 ml chloroacetic acid solution. The absorbance is determined at 505 m_{μ} 1.5 minutes after preparation. If the absorbance is less than 0.10, the test is repeated using 10 ml 0.005? MO or the sample is diluted with chlorine demand-free water and the test repeated.

If manganese is present, a second determination is required. In this case, 0.10 gram 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.

* Methyl Orange Powder, Lot No. 82438, J. T. Baker Chemical Co., Phillipsburg, N. J., was used in this work. Other samples tested gave somewhat different calibration curves but all produced satisfactory results.

To determine total bromine and total 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 (DPD) — pH 6.3

The DPD oxalate test is suitable for the determination of total bromine plus free chlorine. If potassium iodide is added to the sample prior to addition of the sample to the reagent, total bromine and total chlorine can be determined.

The DPD reaction is a color development reaction in the pH range of 6.2 to 6.5> and requires 1.5 minutes for total bromine plus free chlorine, and 5 minutes for total halogen.

The calibration curve is linear in the range from 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 range of 2° to 40°C (Figure 3).

Nitrite ion does not interfere with the DPD test and 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 4). However, if potassium iodide is not added to the sample prior to the mixing of the sample with the reagent and buffer, the DPD response to tribromamine 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.

The ferrous ammonium sulfate (FAS) titration procedure with DPp[3] was evaluated. Chloramine was found to interfere appreciably. This interference was greater during the 1 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.

The procedure for total bromine plus free chlorine 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 complete response will not be obtained.

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

Reagents:

(1) DPD oxalate indicator solution. 1 gram DPD oxalate* is dissolved in ammonia-free distilled water containing 8 ml of 1+3 sulfuric acid and 0.2 gram disodium ethylenediamine tetraacetate dihydrate (EDTA). This solution 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 grams dibasic sodium phosphate and 46 grams 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 gram 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

Procedure:

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 mp in 1.5 minutes.

To determine total halogen (total bromine plus total chlorine), 1 gram 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.

* N,N-Diethyl-p-phenylenediamine Oxalate, No. 7102, Eastman Kodak, Rochester, N.Y., was used in this work.

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. 5 ml of 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 and combined, in concentrations up to 5 mg/1. 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. For the lower bromine concentrations it exhibits a decided curvature which may be due to impurities in the reagent (Figure 5). 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 0.001% PR reagent. The PR buffer has the capacity to produce the proper pH in samples with alkalinity up to 1000 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 4).

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 for bromine concentrations of 0.0 to 0.7 mg/1. 7 drops of 0.1 N sodium hydroxide are added to 50 ml of solution (a) and diluted to 500 ml. The phenol red reagent solutions are stable for one month.

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

(3) Arsenite. 1.0% solution of sodium arsenite

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 and buffer mixture, 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.

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 adjust the pH of samples with an 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 from 2° to 40°C (Figure 6). 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 7).

* Phenol Red, Lot No. 764768 P-74, Fisher Scientific Co., Fair Lawn, N. J., was used in this work. Other samples tested gave similar calibration curves.

Interference from manganic ion, nitrite, and chloramine may be considered negligible. Ferric ion produces a slight, but inconsistent interference (Figure 8).

Free chlorine and bromamine interfere only slightly if arsenite is added 1.0 minute after sample, buffer, and reagent are mixed. The BCP response to monobromamine (prepared at pH 8.8) is less than *1%*, and the response to dibromamine (pH 7.3) and tribromamine (pH 5.0) is about *2%* in one minute (Figure 4).

In the absence of bromide ion, free chlorine produces only a slight interference (about 2.5$ in 1 minute and 6$ in 2 minutes contact time). The addition of sodium arsenite 1 minute after the sample, buffer and reagent are mixed limits further bleaching of the color during measurement of absorption.

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

Reagents:

(1) Brom cresol purple, sodium salt*. 0.0125% solution (the reagent is dried at 105°C for 1 hour prior to weighing). The reagent solution is stable for 1 month.

(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

(4) Bromide. 2.6% solution of sodium bromide

Procedure:

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

* Brom Cresol Purple, Sodium Salt, Catalog No. 342, Allied Chemical Corporation, 40 Rector St., N. Y., N. Y., was used in this work.

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 of buffer and after thorough mixing this solution is added to 1 ml or 3 ml of the 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.

The phenosafranin reagent is bleached by bromine at pH 9.5. The calibration curve covers the range from 0.0 to 10 mg/1 free bromine and does not appear to be temperature dependent in the range from 2° to 40°C (Figure 9).

Manganic ion, ferric ion, nitrite, and chloramine interferences are negligible.

Free chlorine produces a significant interference (about 6% in 1 minute and 9.5% in 2 minutes). Phenosafranin shows nearly the same type of response to the bromamines as does BCP (Figure 4). In the 1 minute contact time before the absorbance is measured, interference from monobromamine (prepared at pH 8.8) is 1%, that from dibromamine (pH 7.3) is about 3%, and that from tribromamine (pH 5.0) is 5%. The sample should be added to the buffer and then this mixture added to the reagent. If arsenite is not added before the absorbance is measured, the bromamine interference increases with time. Free chlorine and bromamine interference may be limited by the addition of a solution of sodium arsenite 30 seconds after the buffered sample is added to the reagent.

Reagents:

(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 5 N sodium hydroxide added per liter

(3) Arsenite. 1.0% solution of sodium arsenite

* Phenosafranin, No. 1125, Eastman Kodak, Rochester, N.Y., was used in this work.

Procedure:

To determine free bromine, a 50 ml sample is added with mixing to 10 ml of buffer. After thorough mixing, this solution is added to 3 ml of the phenosafranin reagent and mixed. After 30 seconds, 1 ml of 1% sodium arsenite is added and mixed. The absorbance is determined at 520 my after 1 minute.

6. Methyl Orange (MO) — pH 9.5

At this high pH, 10 ml of methyl orange standard solution is suitable for the determination of free bromine in concentrations up to 6 mg/1 Br_2.

This test relies on the bleaching effect of bromine on the reagent. The calibration curve is non-linear below 1 mg/1 free bromine and does not appear to be temperature dependent in the range from 2° to 40°C (Figure 10). Nitrite ion does not interfere. Ferric ion and manganic ion do interfere. Ferric ion interference is shown in Figure 11. An arsenite modification was used to determine interference due to manganese. However, the quantity of manganic ion interference is difficult to establish since results are not reproducible. Manganic ion produces a negative interference. The addition of 1 mg/1 Mn^{+++} to samples containing 1.5 to 3.0 mg/1 Br_2 appears to reduce approximately 40% of the apparent free bromine.

Chloramine does not react at this pH, but interference from free chlorine is significant. 1.0 mg/1 of chloramine (as Cl_2) does not react with methyl orange at pH 9.5 and the presence of up to 200 mg/1 bromide ion does not promote a reaction. However, free chlorine reacts to the extent of about 9% in the 1.5 minutes contact time before the absorbance is measured.

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 3% of a dibromamine solution reacts, and about 6% of a tribromamine solution reacts (Figure 4).

Free chlorine and bromamine interference may be limited by the addition of sodium arsenite one minute after the sample-buffer and reagent are mixed.

Visual color comparisons, particularly in the presence of Mn^{+3} or Fe^{+3}, may be difficult since the test color at pH 9.5 is yellow. Since this test does not appear to have any advantages over the other two free bromine tests, BCP and PS, no further applications of the MO pH 9.5 test were thought to be necessary.

Reagents:

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

(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 of buffer. After thorough mixing, this solution is added to 10 ml of methyl orange and mixed. After 1 minute, 1 ml of *1%* sodium arsenite solution is added and absorbance is determined at 464 my at 1.5 minutes.

E. Applications of Test Methods

1. The Breakpoint Reaction for Free Bromine

Curves showing bromine and chlorine breakpoint phenomena for water with an ammonia concentration of 1 mg/1 have been prepared at pH 9.2, 8.4, 7.2, and 4.9 (Figures 12 to 19). The ammonia-bromine reaction appears to be similar to the ammonia-chlorine reaction. The bromamine breakpoint requires 14 mg/1 free bromine, while the chloramine breakpoint requires 6 mg/1 free chlorine for oxidation of 1 mg/1 of NH3. These are equivalent on a molar basis. The bromine-ammonia reaction is generally faster than the chlorine-ammonia reaction, especially at pH 9.2; the reaction of either halogen with ammonia is slow at pH 4.9. It may be observed that amine stability is better for chlorine than for bromine.

* Lot No. 82438, J. T. Baker Chemical Co., Phillipsburg, N. J., was used in this work. No other samples were tested.

Methyl orange and neutral orthotolidine were the reagents used in preparing the chlorine breakpoint curves. Both reagents may be used for the measurement of free and of total residual chlorine. Methyl orange, phenol red, and brom cresol purple were the tests used in preparing the bromine curves. Phenol red with arsenite added at 15 seconds and BCP with arsenite added at 1 minute, were used for the free bromine determinations. Phenol red and methyl orange were used for the determination of total bromine. The PR results for free bromine were higher than the BCP results because bromamines were present in the samples. There is a slight but noticeable reaction between PR and the bromamines in the 15 seconds allowed for free bromine reaction prior to the addition of arsenite. The phenol red test is not recommended for the determination of free bromine in the presence of bromamines.

Samples were prepared by the addition of the desired concentration of free bromine or chlorine to a buffered solution containing NH_3 while mixing on a magnetic stirrer. The samples were stored in glass-stoppered bottles and portions were extracted periodically for analysis. Tests run at a given contact time 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 fourth test. This may account for some variation in results with different tests, especially with short contact times.

2. Studies of Bromamine Stability

A major source of difficulty in working with bromamine solutions stems from their extreme instability. A series of stability tests were carried out at room temperature with varying ammonia to bromine ratios and varying pH.

The test procedure was as follows: Free bromine (as NaOBr) was added to a buffered solution containing the desired concentration of 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 methyl orange procedure. The bromamine species were identified by means of ultra-violet absorption spectra.

Using the works of Galal-Gorchev and Morris [5,6,7] as sources of reference, reasonable confirmation of UV absorption spectra of the bromaraines has been obtained. Absorption maxima were observed at 280 my for monobromamine, at 230 my for dibromamine, and 260 my for tribromamine.

Examination of Figures 20 to 26 reveals that, in general, bromamine stability may be improved by increasing the ammonia-to-bromine ratio, by increasing the pH or by decreasing the temperature. As an example we may consider tests at pH 9.0-9.2 where UV absorption shows bromamine present only as NH_2Br. With ammonia and bromine concentrations of 1000 and 50 mg/1 respectively, the initial bromamine concentration is reduced to 50% after 11.7 hours contact time. With 10 mg/1 of each, the bromamine concentration is reduced to 50% of the initial concentration in 0.9 hours. With ammonia and bromine concentrations of 10 and 50 mg/1, only 50% of the initial bromamine concentration remains after 0.075 hours.

In Figures 23 and 24, the bromamine stability at pH 6 appears improved over that at pH 7. This is due to the presence of tribromamine. In both cases the UV spectra at pH 7 was indistinct, and it is assumed that the bromamine was primarily $NHBr_2$. At pH 6, however, UV absorption showed that a major portion of the bromamine was present as NBr_3. It appears that NH_2Br is the most stable bromamine species, and $NHBr_2$ the least stable as is reported by Galal-Gorchev and Morris [5,6].

3. The Reaction of Bromide Ion with Chloramine

The addition of bromide ion to a chloramine solution reduced chloramine stability (Figure 27), apparently due to the formation of bromamine. In general, solutions of chloramine and bromide ion exhibit the stability characteristics of bromamine solutions, i.e., their stability depends on initial conditions such as ammonia-to-bromine (in this case in the form of bromide ion) ratios and pH. The effects of pH, ammonia and bromide ion concentrations, temperature, and contact time are discussed in the following section.

4. The Reaction of Chlorine with Buffered Solutions Containing Ammonia and Bromide Ion

In studies of the reaction of chlorine with solutions containing ammonium and bromide ions, four of the five recommended colorimetric methods have been used for the

determination of bromine, bromamine, chlorine, and chloramine. The effects of initial conditions such as pH, ammonium and bromide ion concentrations, temperature, and contact time have been examined in order to determine their relation to the proportion of chloramine and bromamines resulting.

The buffer solutions used for preparation of the samples are listed at the end of this section. Free chlorine (either 2.0 or 3.0 mg/1) was added to buffered samples containing either 0.5 mg/1 or 4 mg/1 ammonia (from ammonium chloride) and sodium bromide. The bromide ion concentrations were 3, 5, and 25 mg/1. The pH values ranged from 4 to 9. The temperatures were 26°C and 10°-15°C. At 2, 5, or 10 minutes after the addition of chlorine, portions of each sample were removed and a series of tests was run as nearly simultaneously as possible (Figures 28 to 33). The brom cresol purple reagent was used to determine free bromine residuals. Phenol red was used to determine total bromine exclusive of chlorine. Methyl orange reagent with bromide added to the final mixture, and DPD oxalate with prior addition of potassium iodide to the sample, were used to determine total halogen (total bromine and total chlorine). The phenosafranin reagent was not tested because of its lesser sensitivity and because its behavior is similar to that of the brom cresol purple reagent.

For chlorinated samples at 26°C containing 4.0 mg/1 NH_3 (Figures 29 and 3D and 3, 5, and 25 mg/1 Br", the BCP test results show that negligible quantities of free bromine were formed. Any apparent response is probably due to interference from bromamines in the one minute of contact prior to the addition of arsenite. For these same samples, the phenol red test results indicate that bromamines are the primary species formed at a pH value of 4.3; results of the MO and DPD tests for total halogen at this pH agree with the PR results. As the sample pH is increased beyond pH 4.3, the PR results indicate that the concentrations of bromamine decrease and the rate of decrease is greater for decreasing bromide levels. For these chlorinated samples containing 4 mg/1 NH_3, the concentration of bromide ion and the sample pH have little effect on the final concentration of total halogen formed, as shown by the MO and DPD results, which are in good agreement.

For chlorinated samples at 26°C containing 0.5 mg/1 NH_3 (Figures 28, 30, and 32) the BCP test again indicates only negligible quantities of (apparent) free bromine were formed. The PR, MO, and DPD test results for samples of pH 4.3 again show that bromamines are the predominant species. For pH values greater than 4.3, the PR results indicate decreasing

concentrations of bromamines. The MO and DPD tests for total halogen show that at pH 7.4 the concentration of total halogen formed in the presence of 25 mg/1 Br~ is considerably lower than that formed in the presence of 3 and 5 mg/1 Br^-. Phenol red test results do indicate that some bromamine is formed under these conditions; so apparently the bromamine species formed at pH 7.4 is predominately unstable dibromamine.

An examination of Figure 33 shows that at 10°- 15°C and in the presence of 25 mg/1 Br", bromamines are the primary species formed at a pH value of 4.3. As the sample pH is increased beyond pH 4.3, the concentration of bromamines decreases. For the entire range of pH values tested, the concentration of bromamine formed in the presence of 3 and 5 nig/1 Br^- was considerably lower than that formed in the presence of 25 mg/1 Br^-.

These studies indicate that the reaction to form bromamines is highly pH dependent. In solutions containing Br^-, NH3, and 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 a high pH value and 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 lower values.

Buffer Solutions:

(1) Buffer pH 4.3. 9 ml glacial acetic acid and 4.102 grams sodium acetate, anhydrous (0.5 M) per 100 ml (0.5 ml buffer was added per 500 ml sample).

(2) Buffer pH 5.4. 80 ml 0.5 M sodium acetate and 16 ml 0.5 M acetic acid are combined. (1 ml buffer was added per 500 ml sample).

(3) Buffer pH 7.3. 35 grams dibasic sodium phosphate and 17 grams monobasic potassium phosphate are dissolved in ammonia-free distilled water and diluted to 1 liter. (5 ml buffer was added per 500 ml sample).

(4) Buffer pH 9.2. 0.042 M borax
(5 ml buffer was added per 500 ml sample).

5. Bromine Demand of Ammonia and Amino Acids

The five selected colorimetric procedures for the determination of free and combined bromine were evaluated for their performance in water containing ammonia and amino acids. The five reagents are DPD oxalate, methyl orange (pH 2), phenol red, brom cresol purple, and phenosafranin. Breakpoint curves were determined by these methods and the curves were compared with similar curves determined by two different amperometric titration procedures — the standard amperometric method and a method proposed by Johannesson[2]. In this report, the latter will be referred to as Johannesson's amperometric titration method.

The water used for these tests was ammonia-free distilled water and contained 150 mg/1 each of alkalinity and hardness (see Appendix 1, section VI). The pH of the water was adjusted with carbon dioxide and then was used in preparing the brominated samples of ammonium chloride, glycine, and L-cystine.

For each sample the nitrogen (N) concentration was 0.3 mg/1. The pH of each sample was adjusted to 6.5, 7, or 8. The temperature of the samples was 26°C (room temperature). The reaction times were 1 hour and 24 hours.

Varying concentrations of bromine were added to the ammonia and amino acid samples and after the 1 hour and 24 hours reaction times, free and total residual bromine were determined by the appropriate tests. Free residual bromine was determined by the brom cresol purple, phenosafranin, and Johannesson's amperometric titration methods. Total residual bromine was determined by DPD (with prior addition of KI to the sample), methyl orange, phenol red, standard amperometric titration and, where applicable, by Johannesson's amperometric titration procedure.

As was briefly explained in the Introduction, section IV. A. of this report, when using Johannesson's amperometric titration procedure one has to first accept the assumption that the free and combined forms of bromine do not coexist. The method provides a measure of total bromine only, with an indication as to whether or not any free bromine is present.

Therefore, in this study, results obtained with this method were presented as total bromine prior to the breakpoint, and free bromine beyond the breakpoint where evidence of some free bromine was consistently obtained. In Figures 34, 35, and 38, where the breakpoint reaction is apparent, the values were plotted as total bromine and, beyond the breakpoint, also as free bromine. In Figure 39, only the DPD method indicates the presence of combined bromine before the breakpoint. Apparently some organic bromine compounds are also formed in the reaction between bromine and glycine and these compounds react with DPD.

The ammonium chloride samples were prepared only at pH 7.0-7.5. As shown in Figures 34 and 35 the breakpoint for these samples occurs at a free bromine dosage of 6.5 mg/1, corresponding to a Br:N mol ratio of 3.8. All tests for free and total residual bromine are in reasonably good agreement. Agreement is improved at the longer reaction time of 24 hours, Figure 35.

Glycine-bromine samples were prepared at pH values of 6.5 and 8.0 (Figures 36 to 39). There is no evidence of bromamine formation before the breakpoint at the lower pH. Samples having a pH of 8 (Figures 38 and 39) showed a breakpoint at a dosage of 11 mg/1 free bromine, corresponding to a Br:N mol ratio of 6.43. At the 1 hour reaction time, the DPD values for total residual bromine were considerably higher than the values determined by the other tests. There was also so much scatter of points that it is impossible to draw a curve for DPD in Figure 36. In addition, the DPD reaction with samples of pH 8 before the breakpoint was extremely unstable. The color increased rapidly thus indicating a definite reaction between DPD and some products of the bromination of glycine. Agreement among the other tests for total residual bromine is good. All three tests for free bromine are in good agreement with one exception. As shown in Figure 36 Johannesson's amperometric titration values for free bromine are considerably higher than results by BCP and phenosafranin.

L-cystine-bromine samples were prepared at pH values of 6.5 and 8 (Figures 40 to 43). There is no evidence of bromamine formation before the breakpoint at these pH values. Agreement among the tests for free and total bromine is rather poor at the 1 hour reaction time but is somewhat improved after 24 hours reaction time. In the concentration range of free bromine added samples having a pH of 8 (Figures 42 and 43) showed no free bromine residual remaining after 24 hours reaction time; all the bromine residual remaining is in the combined form.

It can be concluded from this study of the bromine demand of ammonia and amino acids that in general the values for free residual bromine determined by brom cresol purple, phenosafranin, and Johannesson's amperometric titration were in good agreement. The DPD test results were consistently higher than the methyl orange (pH 2), phenol red, standard amperometric titration, and Johannesson's amperometric titration results for total residual bromine. Agreement among all the tests for free and total bromine improved at the 24 hours reaction time.

6. Bromine Demand of Activated Sludge and Primary Effluent Solutions

The brom cresol purple, phenosafranin, DPD oxalate, methyl orange (pH 2), phenol red, Johannesson's amperometric titration, and the standard amperometric titration procedures were evaluated for their performance in highly polluted water.

Solutions of activated sludge or primary effluent were prepared in ammonia-free water containing 150 mg/1 each of alkalinity and hardness (see Appendix 1, section VI), and adjusted to pH 7. The temperature of the samples was 26°C (room temperature). The contact times were 1 hour and 2 hours.

Varying concentrations of bromine were added to dilutions of activated sludge and primary effluent and, after the desired contact times, free and total residual bromine were determined by the proper tests. Free residual bromine was determined by the BCP, PS, and Johannesson's amperometric titration tests; total residual bromine was determined by the DPD (with prior addition of KI to the sample), MO, PR, and both amperometric titration methods. Representative results of these studies are given in Figures 44 through 49. It should be noted that two separate studies were made. In the first study the standard amperometric titration was not evaluated (Figures 44 through 47). In the second study, this method was included in the evaluation; the phenol red and phenosafranin tests were not (Figures 48 and 49).

The BCP, PS and Johannesson's amperometric titration values for free residual bromine were in reasonably good agreement. Agreement among the tests for total residual bromine, in particular prior to the breakpoint, was unsatisfactory. The DPD test gave the highest total residual bromine values followed by standard amperometric titration, MO, PR, and Johannesson's amperometric titration, in that order.

In general, the MO and standard amperometric titration determinations were in reasonably close agreement. The differences in the resulting total residual bromine values were more pronounced with the primary effluent samples (Figures 46, 47, 49) than with the activated sludge effluent samples. The contact time did not appear to alter any of these relationships.

In this study of sewage effluents, in every case varying concentrations of combined bromine were formed before the breakpoint and varying concentrations of free bromine were formed beyond the breakpoint. As was done previously in section #5, the values for Johannesson's amperometric titration method were plotted as total bromine in each Figure and the values beyond the breakpoint were plotted also as free bromine.

F. Free Bromine and Bromide Ion Tests for Shipboard Use

Available test methods have been considered for possible adaptation to shipboard use by the Navy in analyzing water for bromine and bromide ion. It has been assumed that visual comparison with standards would be the method of reading and that the concentrations of interest were 1 mg/1 of free bromine and 20 mg/1 of bromide ion. The BCP test is the only test found to be adaptable to the determination of bromine and bromide ion under these conditions.

In the BCP method for free bromine, reagent quantities have been modified so that visual comparison with standards in the 0.8-1.2 mg/1 range is facilitated. The standards represent the residual color after bleaching by 0.8-1.2 mg/1 bromine. A dilute reagent is used so that the colors produced are rather pale and easily compared. Ferric ion in concentrations up to 0.7 mg/1 will not significantly distort the pale purple BCP test color.

In the BCP method for bromide ion, the bromide ion in a 1:10 dilution of the sample can be oxidized with free chlorine at pH 3.0, and the resulting free bromine determined by BCP. After one minute reaction time, the excess free chlorine is reduced with sodium arsenite and comparison made with a 4 mg/1* free bromine standard. If the resulting color

* The 4 mg/1 standard and 1:10 dilution is required because one equivalent of bromide ion Is oxidized to one mole of hypobromite which corresponds to two equivalents of free bromine.

$$Br_2 + H_2O \rightarrow HBr + HOBr$$

$$Br^- + Cl_2 + H_2O + H^+ \rightarrow 2HCl + HOBr$$

is deeper than that of the standard then the water under test contains less than 20 mg/1 bromide ion. If the resulting color is paler than that of the standard then the water under test contains more than 20 mg/1 bromide ion and a smaller portion of the sample should be removed and tested again.

The free bromine present in the sample will be included in the determination of bromide ion. However, in a 1:10 dilution the. concentration of free bromine will normally be negligible. In such a dilution the effect of Fe^{+3} and Mn^{+3} color interference will also be reduced.

The dilution must be made only with ammonia-free distilled water. In the presence of even 0.1 mg/1 ammonia in the distilled water, only 65-70% of the bromide ion is recovered in this determination. This is probably due to the formation of broma-mines which do not react with the BCP reagent.

G. Manganese Interference Study

In checking the interference due to the manganic ion in the brom cresol purple and phenol red tests, no manganese interference was observed when Br_2 was not present in the sample. However, in samples containing both bromine and manganese, there appeared to be negative interference due to manganese. The same effect was observed when free bromine was determined by means of the arsenite modification of the DPD test on a sample containing both bromine and manganese.

It may be shown that free bromine oxidizes Mn^{+2}. This was checked using the phenol red test. A sample of Mn^{+2} and Br_2 of known concentrations in buffered solutions was prepared and the sample tested periodically for loss of Br_2. At pH 5.1 and pH 6.2, free bromine did not oxidize Mn^{+2}. However, at pH 8.4 and above, free bromine in moderate excess slowly oxidized the manganese ion. The product of this oxidation is not entirely Mn^{+4}.

Since the manganic ion was prepared for use in these tests by air oxidation at pH 10, it appears probable that the negative interference found in the phenol red and brom cresol purple methods was not a true interference but a consumption of bromine in further oxidation of the manganese ion at the high pH used in the test.

Several methods of removing manganese prior to analysis were investigated. All methods tested which remove manganese also remove bromine.

H. Summary of Results

In this study twenty-seven reagents have been evaluated for possible use in the determination of free and combined bromine. Ideally, the methods 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 the 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	TEST pH	RESIDUALS DETERMINED
Methyl Orange	2	Cl_2+Br_2+ Bromamine
Methyl Orange + Br^-	2	Cl_2+Br_2+ Bromamine + Chloramine
DPD Oxalate	6.3	Cl_2+Br_2+ Bromamine
DPD Oxalate + KI*	6.3	Cl_2+Br_2+ Bromamine + Chloramine
Phenol Red	5	Br_2+ Bromamine
Brom Cresol Purple**	9.5	Br_2
Phenosafranin***	9.5	Br_2
Methyl Orange**	9.5	Br_2

* KI is premixed with sample.
** Arsenite is added 1 minute after buffered sample and reagent are mixed.
*** Arsenite is added 30 seconds after buffered sample and reagent are mixed.

Free bromine calibration curves for DPD oxalate, phenol red, brom cresol purple, phenosafranin, and methyl orange (pH 9.5) do not show temperature dependence. Methyl orange (pH 2) shows a slight temperature dependence In the range 2 to 40°C. The PR calibration curve exhibits a decided curvature for bromine concentrations below 1.5 mg/1. The BCP calibration curve is non-linear below 1 mg/1 Br_2.

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

Breakpoint data show that the bromine breakpoint requires 14 mg/1 free bromine, while the chlorine breakpoint requires 6 mg/1 free Cl_2 for oxidation of 1 mg/1 of NH_3. The bromine - ammonia reaction is generally faster than the chlorine - ammonia reaction, especially at pH 9.2; the reaction of either halogen with ammonia is slow at pH 4.9. The bromamines are considerably less stable then the chloramines but in general stability can be improved by increasing the N:Br ratio, increasing the pH and decreasing the temperature. However, below pH 6, decreasing the pH promotes tribromamine formation, Improving stability. Absorption maxima were observed at 280 my for monobromamine, at 230 my for dibromamine, and at 260 my for tribromamine.

The BCP, PR, MO (pH 2), and DPD oxalate tests were used to study the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide for varying contact times and at temperatures of 26°C and 10°-15°C.

The BCP reagent was used to determine the presence of any free bromine. Phenol red determined total bromine only, while MO with bromide added and DPD with prior addition of KI to the sample determine total halogen.

Results from this study indicate that bromamine formation is dependent primarily upon pH. 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.

Chloramines are apparently the primary species formed at pH values greater than 7 and do not react with bromide ion. If the bromide ion is present, differentiation of chloramine and bromamine is not possible by the PR, MO, and DPD tests. At pH values less than 7 chloramine reacts with bromide ion to form some bromamine.

In waters containing ammonia and amino acids, free residual bromine values determined by brom cresol purple and phenosafranin reagents were in good agreement.

In dilutions of activated sludge and primary effluents, free residual bromine values determined by the BCP and PS methods were in fairly good agreement. Agreement between the DPD, MO (pH 2), and PR tests for total residual bromine was unsatisfactory. This was particularly noteable prior to the breakpoint and in the presence of a high degree of organic pollution.

The DPD test gave consistently higher results than either of the two amperometric titration tests, the MO, or PR tests. Apparently organic bromamines are formed and the DPD reagent is sensitive to these compounds. As the concentration of pollutants is increased there is a corresponding increase in the concentration of organic bromamines formed.

The BCP test appears to be adaptable to a visual comparison procedure for the determination of free bromine. Reagent quantities have been modified so that visual comparison with standards in the 0.8-1.2 mg/1 Br_2 range is facilitated.

The bromide ion in a 1:10 dilution of the sample can be oxidized with free chlorine at pH 3.0 and the resulting free bromine determined by visual comparison with a BCP standard.

I. Conclusions

The major objective of this project has been the development of suitable analytical methods for the determination of free bromine and of bromamines in water. Ideally, the methods should be capable of differentiating between free bromine, free chlorine, bromamines, and chloramines. The methods should be suitable for use in polluted waters and free of interference from the substances normally found in such waters. In addition, the methods should be suitable for field use.

A second aim, essential to the above, has been the examination of the basic chemistry of bromine in water, particularly its reaction with ammonia and amino compounds.

A third concurrent aim has been the examination of the reaction of chlorine with ammonia in the presence of bromide ion.

It is possible that free bromine, free chlorine, bromamines, and chloramines may be distinguished from one another. Free bromine alone may be determined by the brom cresol purple or phenosafranin tests. PS is the less sensitive of the two tests. Phenol red is a unique test for total bromine. The DPD and MO tests may be used to determine total bromine plus free chlorine. The DPD oxalate test serves well to indicate total halogen (total bromine plus total chlorine), if potassium iodide is added to the sample. The methyl orange (pH 2) test is also suitable for the determination of total halogen, in the presence of bromide ion. The Department of the Navy has expressed an interest in using the BCP test for free bromine and bromide ion determination for shipboard use. These testing procedures have been submitted to them. It appears probable that the BCP test can be modified so that the free bromine and bromide ion concentrations may be determined by visual comparison with standards.

Breakpoint curves for both chlorine and bromine indicate more rapid reaction of bromine than chlorine, especially at high pH, and emphasize the lack of stability of bromamine as compared with chloramine.

In a study of the bromine demand of amino acids and of activated sludge and primary effluent it was found that the DPD test results were consistently higher than the standard amperometric, Johannesson's amperometric titration, MO (pH 2), and PR test results. The DPD reagent is apparently oxidized by the products of the reaction, probably organic bromamines; but apparently these compounds have less effect on the other four methods used for the determination of total bromine.

It can be concluded from this study of colorimetric tests that BCP is the best test for the determination of free bromine and DPD with prior addition of KI to the sample is the best test for the determination of total halogen. The MO (pH 2) test with bromide added is quite acceptable for

the determination of 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 phenol red test is a unique test for total bromine but did not perform as well in polluted water as was expected and gave lower results than the DPD and MO tests.

Since these methods give different results in polluted waters, it will be essential in any work on disinfection that the method used for determining residuals be specified. Otherwise, correlation of results will be impossible.

It can be concluded also, from studies of the reaction of chlorine with solutions containing bromide ion and ammonia 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.

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VI. APPENDIX 1

A. Preparation of Stock Solutions

All solutions were prepared using bromine, chlorine demand-free water unless specified otherwise.

1. Bromine stock solution: One ml of liquid bromine was added to 15 ml 20% NaOH and about 450 ml water. The solution was mixed to dissolve the bromine and then diluted to 500 ml and stored in a glass-stoppered bottle away from light. A new solution was prepared every two weeks. The bromine solution contained about 5% bromate initially and little change in bromate concentration was observed during a two week period. Each morning a standard free bromine solution was prepared by dilution of the stock bromine solution and standardized by iodometric titration against sodium thiosulfate. (The sodium thiosulfate solution was standardized every 7 days against primary standard 0.025 N potassium dichromate). The procedure for the standardization of free bromine may be found in the section "Standardization Procedures."

2. Bromamine stock solutions: These solutions were prepared by adding 3 mg/1 of a standardized bromine stock solution, with thorough mixing, to buffered ammonium chloride solutions and then diluting to a final volume of 200 ml. The resulting 200 ml sample contains 0.6 mg of free bromine.

a. Monobromamine (NH_2Br). 5 ml of 0.042 M borax, 12 ml of 1,000 mg/1 NH_3 stock (from NH_4Cl), and 3 mg/1 Br_2 were added in the order listed, with mixing, and the solution was diluted to 200 ml. The resulting sample had a NH_3:Br ratio of approximately 20:1 by weight and a pH of 8.8. Ultra violet absorption indicated that the sample contains only monobromamine.

b. Dibromamine ($NHBr_2$). 1 ml of pH 7 phosphate buffer (35 g Na_2HPO_4, 17 g KH_2PO_4, and 20 mg $HgCl_2$ per liter), 6 ml of 100 mg/1 NH_3 stock (from NH_4Cl), and 3 mg/1 Br_2 were added in the order listed, with mixing, and the solution was diluted to 200 ml. The resulting sample had a NH_3:Br ratio of approximately 1:1 by weight and a pH of 7.3. UV absorption indicated that the sample is a mixture of NH_2Br and $NHBr_2$. Dibromamine solutions cannot be prepared free of both NH_2Br and NBr_3 (tribromamine).

c. Tribromamine (NBr_3). 0.5 ml of pH 5 acetate buffer (150 ml of 0.5 M $NaC_2H_3O_2$ and 100 ml of 0.5 M CH_3COOH), 2 ml of 100 mg/1 NH_3 stock (from NH_4Cl), and 3 mg/1 Br_2 were added in the order listed, with mixing, and the solution was diluted to 200ml.

The resulting sample had a NH_3:Br of 1:3 by weight and a pH of 5. UV absorption indicated that the sample contains both NBr_3 and a small quantity of hypobromite (OBr^-).

Bromamine solutions were prepared as indicated above to check bromamine response with the proposed reagents. Solutions of greater bromamine concentrations may be prepared by increasing the NH_3 and NaOBr concentrations while maintaining the same weight ratio.

Since the bromamine solutions were very unstable, at the time each bromamine sample was used an identical sample was tested with methyl orange. The results of this test were used as a measure of the total bromamine present at that time.

3. Chlorine stock solution: A standard free chlorine solution was prepared each morning by dilution of Clorox (5.25% NaOCl) and standardized iodometrically against sodium thiosulfate.

4. Chloramine stock solution: The solution was prepared from 109.2 mg/1 ammonium chloride and 1 ml clorox with 168 mg/1 sodium bicarbonate to adjust pH to 7.8-8.2. The solution was allowed to stand for at least 12 hours (overnight), then standardized immediately before use by the methyl orange test. Such a solution was exclusively monochloramine. The N:C1 ratio was approximately 1:2 by weight.

5. Nitrite solution: Nitrite solution was prepared using sufficient $NaNO_2$ to yield 500 mg/1 nitrite ion.

6. Manganic ion solution: A stock solution of $MnSO_4 . H_2O$ was prepared and standardized colorimetrically. Prior to use (maximum time, 1 hour), the pH was adjusted to 10 with NaOH and, after 10 minutes, neutralized with H_2SO_4. The maximum concentration of manganese which could be oxidized without precipitation was 6.7 mg/1.

7. Ferric iron solution: A stock solution of $FeCl_3.6H_2O$ with 168 mg/1 $NaHC0_3$ added, was prepared and standardized by the phenanthroline method.

8. Sewage polluted water was prepared as follows: A water free of ammonia and containing 150 mg/1 alkalinity and hardness was prepared by adding 84.01 mg $NaHC0_3$, 60.19 mg $MgSO_4$, and 74.1 mg $Ca(OH)_2$ per liter to bromine, chlorine demand-free distilled

water, and adjusting the pH to 7.0 with carbon dioxide. Primary, or activated sludge, effluent was added in concentrations of 2, 5, or 10% by volume. Immediately after bromination the sample pH was adjusted to 7.0 with dilute sulfuric acid. Ammonium ion and COD concentrations were determined as soon as possible after the sewage samples were collected.

B. Standardization Procedures

1. Free Bromine Solution: To determine free bromine (OBr^-) a 200 ml sample was added to about 3 g KI crystals and mixed gently. Then 1 ml glacial acetic acid was added to reduce the pH to 4.0 and the solution was titrated iodometrically against $Na_2S_2O_3$ to a starch endpoint. (The $Na_2S_2O_3$ had been previously standardized against 10 ml of .025 N $K_2Cr_2O_7$). To determine total bromine ($0Br^-$, BrO_2^-, BrO_3^-) 2 ml of 20% Br^- solution and 8.3 ml concentrated HC1 were substituted for the glacial acetic acid to reduce the pH to 0.5. The resulting solution was titrated iodometrically just as for free bromine.

2. Free Chlorine Solution: To determine free chlorine ($OC1^-$), a 200 ml sample was added to about 3 g KI crystals and mixed gently. Then 0.5 ml glacial acetic acid was added to reduce the pH to 4.0 and the solution was titrated iodometrically with previously standardized $Na_2S_2O_3$ to a starch endpoint .

3. Bromamine Solutions: The methyl orange test was used in the quantitative determination of bromamine, but did not distinguish between the 3 forms. UV absorption was used to determine which species was present (i.e., a maximum at 280 my, indicated NH_2Br; at 230 my, $NHBr_2$; and at 260 and 330 my, NBr_3). No procedure has been available for the quantitative determination of a single species.

VII. APPENDIX 2

2 Tables

49 Figures

TABLE 1. REAGENTS CONSIDERED UNSATISFACTORY AFTER PRELIMINARY SCREENING

	BENZIDINE	BROMPHENOL BLUE	CHLORPHENOL RED	CRESOL RED	DIPHENYL-BENZIDINE[1]	EVANS & TRYPAN BLUE[2]	FERROIN	LEUCO CRYSTAL VIOLET	METHYL RED[3]	N,N-DIMETHYL-P-PHENYLENE-DIAMINE[4]	NEUTRAL RED[5]	SULFANILIC ACID-PYRIDINE[6]	TETRAKIS[7]	THYMOL BLUE
DOES NOT CONFORM TO BEER'S LAW	●			●		●		●						●
NOT SENSITIVE TO Br_2		●	●				●							
FREE Cl_2 INTERFERENCE	●			●		●		●	●	●	●	●		
CHLORAMINE INTERFERENCE	●							●	●	●	●	●	●	
BROMAMINE INTERFERENCE						●		●	●	●	●	●		
REAGENT NOT STABLE IN SOLUTION					●									
TEST COLOR NOT STABLE					●	●	●	●				●		
OTHER INTERFERENCES									Mn^{+3}	Mn^{+3}	Mn^{+3}		NO_2^-	

● INDICATES BASIS FOR REJECTION

[1] REAGENT HIGHLY UNSTABLE. GOOD LESS THAN ONE DAY TEST COLOR NOT STABLE LONG ENOUGH TO MAKE DETERMINATION

[2] BOTH REAGENTS DEMONSTRATE SHIFTING WAVE LENGTHS IN DIRECTION OF THE VIOLET RANGE (560 - 570 mμ)

[3] REJECTED EARLIER ON Cl_2 TEST. SIMILAR TO METHYL ORANGE BUT NOT AS GOOD

[4] REJECTED EARLIER ON TEST FOR FREE Cl_2. SIMILAR TO DPD OXALATE BUT NOT AS GOOD.

[5] REJECTED EARLIER ON Cl_2 TEST

[6] SLOW REACTION TIME (6 MINUTES) TEST NOT REPRODUCIBLE

[7] REJECTED EARLIER ON Cl_2 TEST

TABLE 2. REAGENTS NOT UNDER CONSIDERATION AT PRESENT

	DPD OXALATE	ACID OT	BROM CRESOL GREEN	BROM THYMOL BLUE	INDIGOTETRA-SULFONIC ACID	METHYLENE BLUE	NEUTRAL OT	NILE BLUE A
FREE Cl_2	●	●	●	●	●	●	●	●
CHLORAMINE	●	●	●	●				
BROMAMINE	●	●	●	●	●	●	●	●

● INDICATES INTERFERENCE

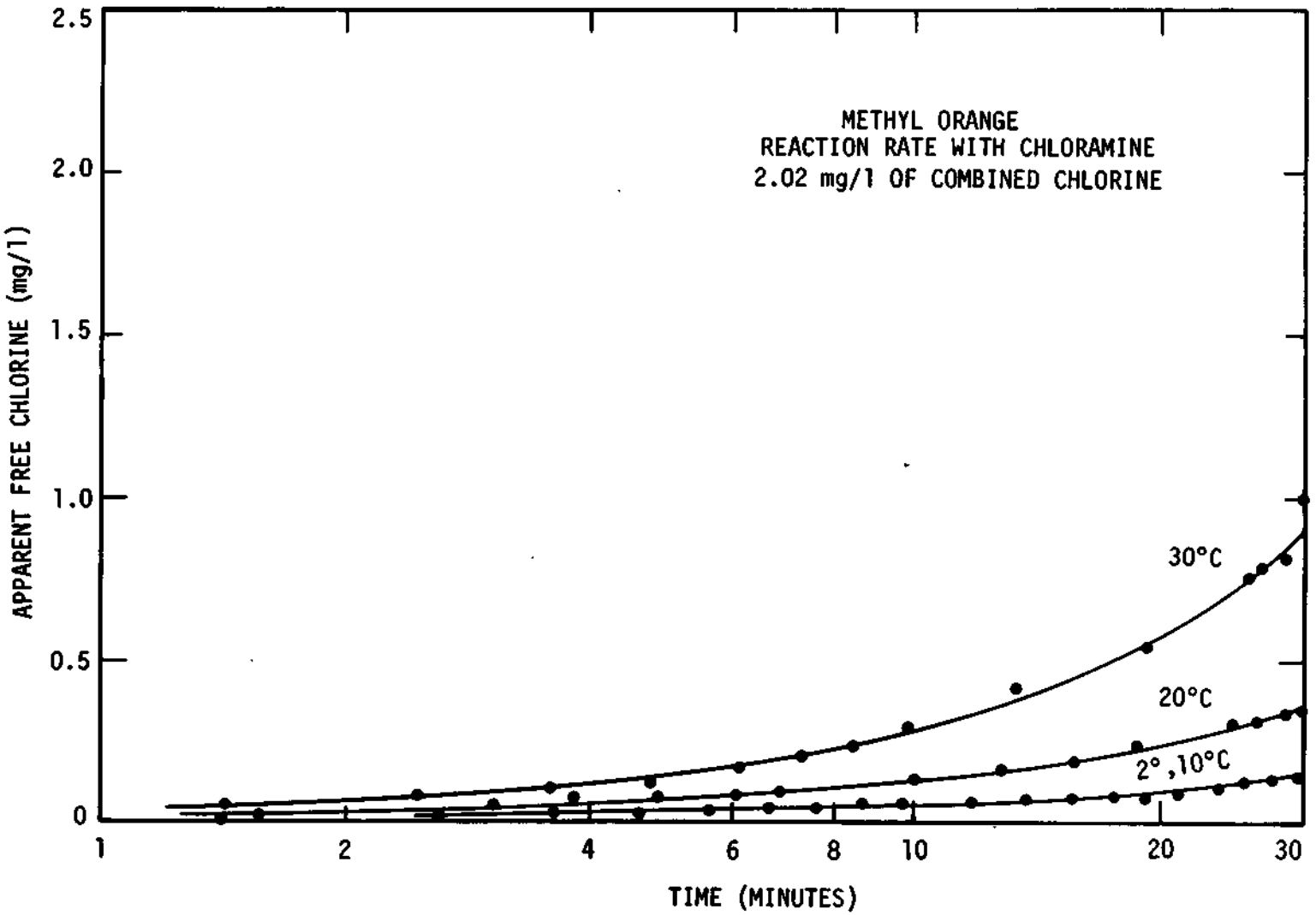

METHYL ORANGE
REACTION RATE WITH CHLORAMINE
2.02 mg/l OF COMBINED CHLORINE
APPARENT FREE CHLORINE (mg/l)
2.5
2.0
1.5
1.0
0.5
0
30°C
20°C
2°,10°C
1
2
4
6
8
10
20
30
TIME (MINUTES)

Figure 1

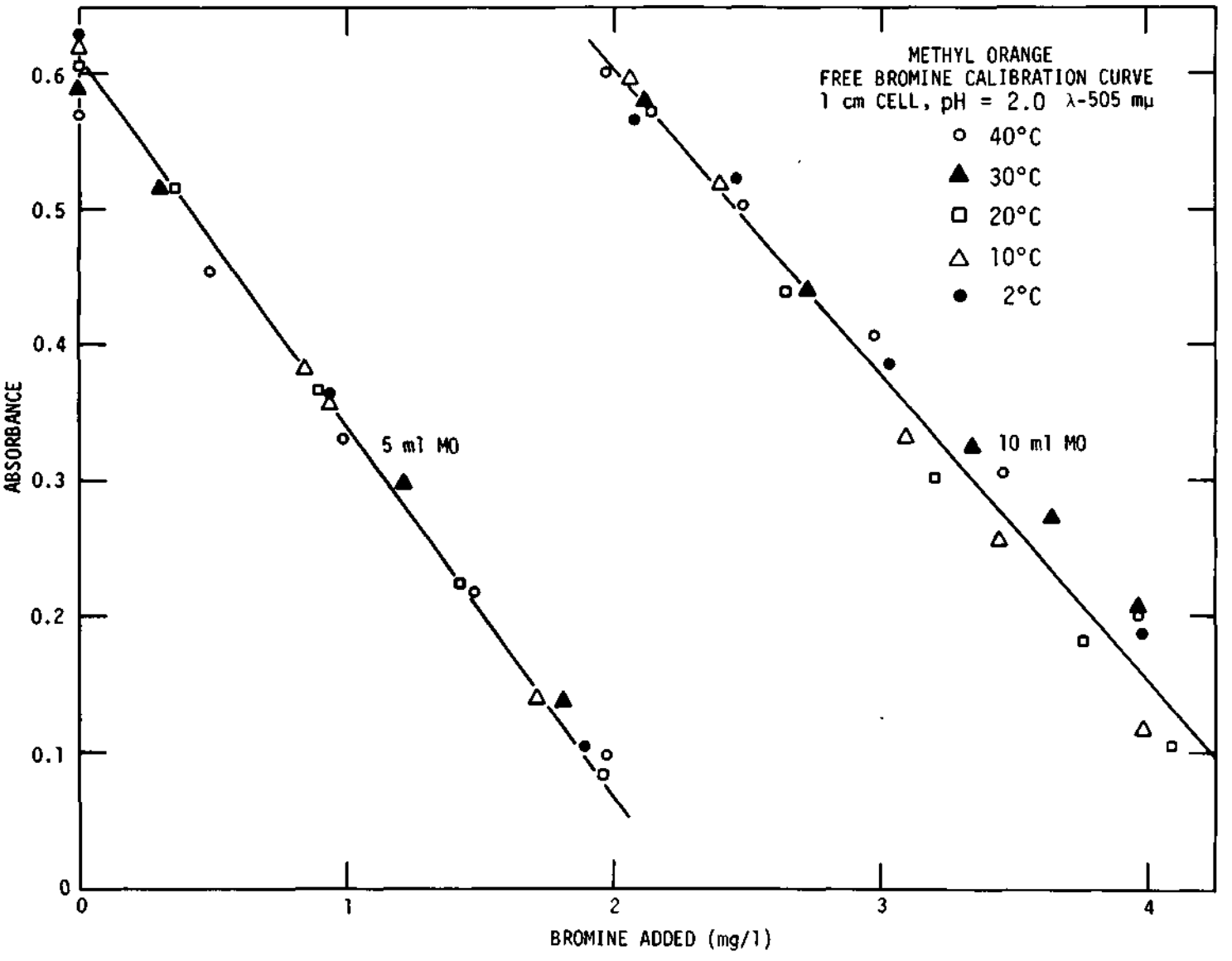

METHYL ORANGE
FREE BROMINE CALIBRATION CURVE
1 cm CELL, pH = 2.0 λ-505 mμ
40°C
30°C
20°C
10°C
2°C
5 ml MO
10 ml MO
ABSORBANCE
BROMINE ADDED (mg/l)
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3
4

Figure 2

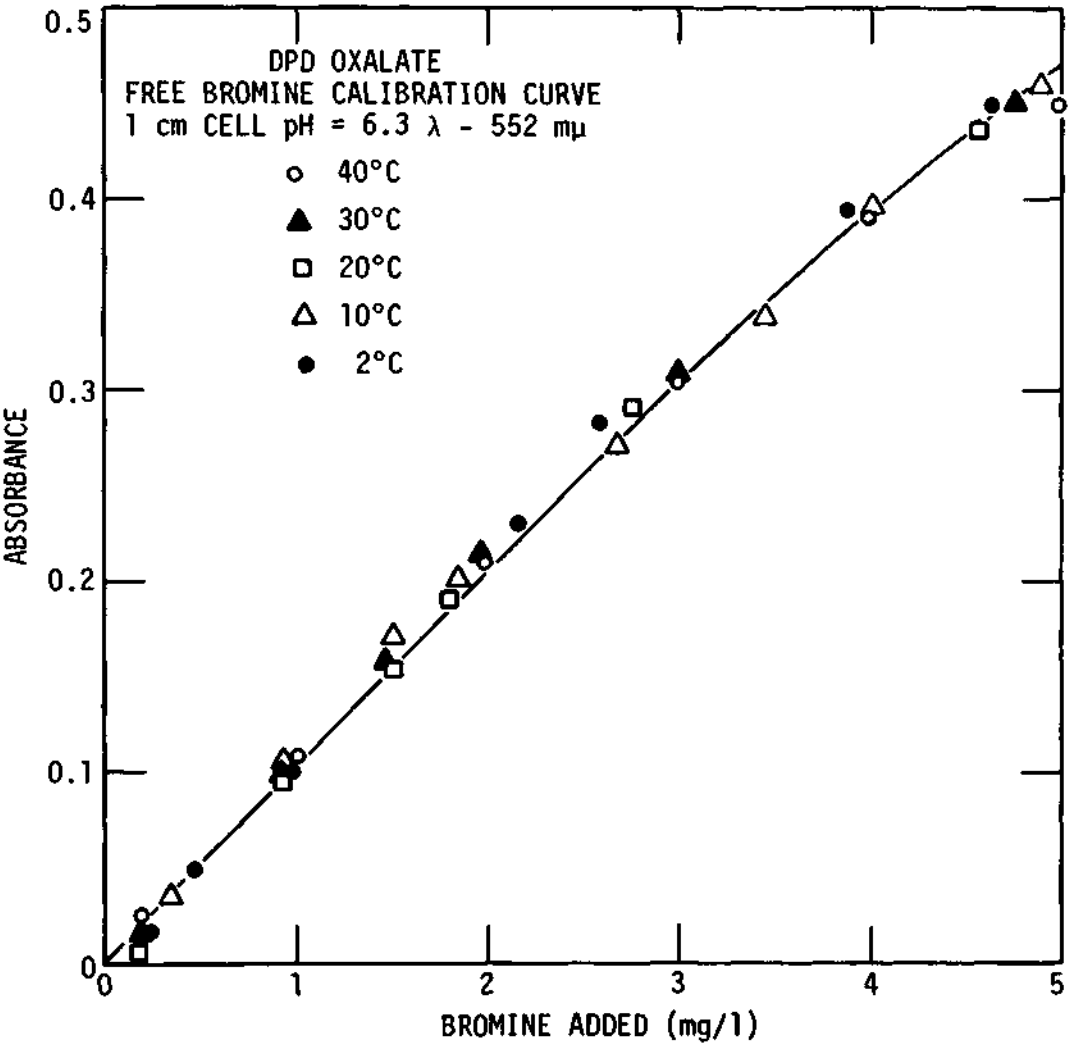

DPD OXALATE
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 6.3 λ - 552 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
BROMINE ADDED (mg/l)
0
0.1
0.2
0.3
0.4
0.5
1
2
3
4
5

Figure 3

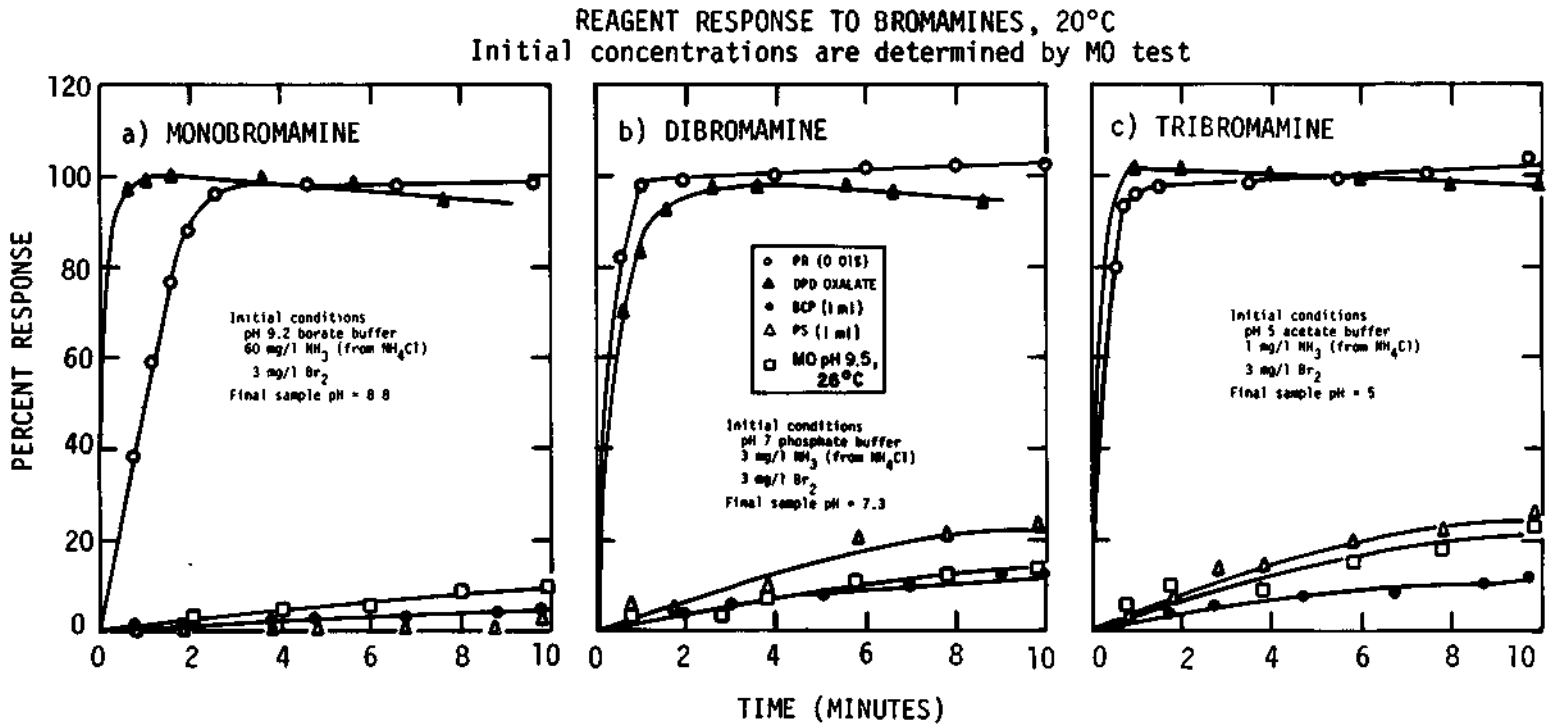

REAGENT RESPONSE TO BROMAMINES, 20°C
Initial concentrations are determined by MO test
a) MONOBROMAMINE
b) DIBROMAMINE
c) TRIBROMAMINE
PERCENT RESPONSE
TIME (MINUTES)
PR (0 OIS)
DPD OXALATE
BCP (1 ml)
PS (1 ml)
MO pH 9.5, 26°C
Initial conditions
pH 9.2 borate buffer
60 mg/l NH3 (from NH4Cl)
3 mg/l Br2
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 4

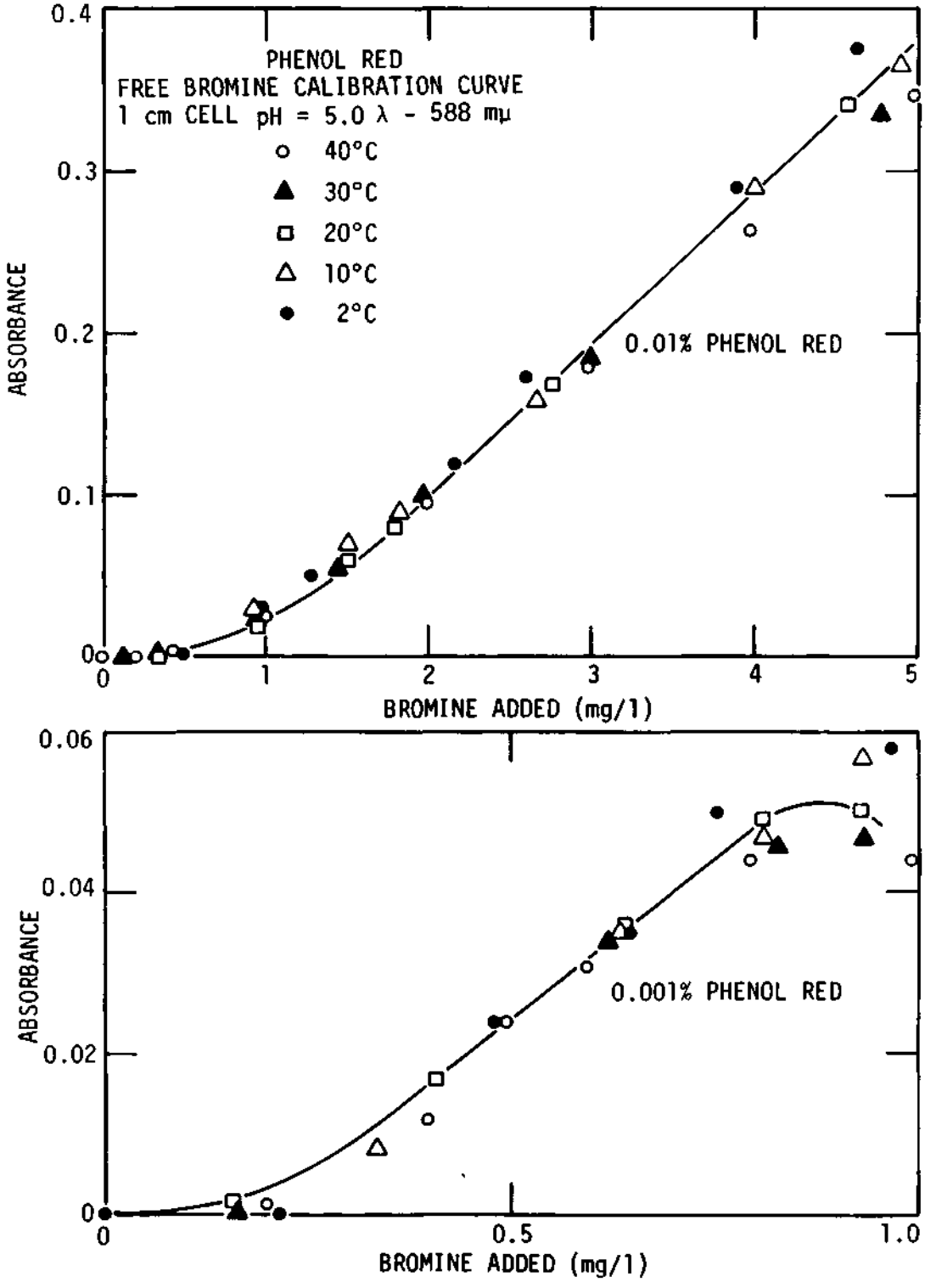

PHENOL RED
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 5.0 λ - 588 mμ
40°C
30°C
20°C
10°C
2°C
0.01% PHENOL RED
ABSORBANCE
BROMINE ADDED (mg/1)
0.001% PHENOL RED
ABSORBANCE
BROMINE ADDED (mg/1)

Figure 5

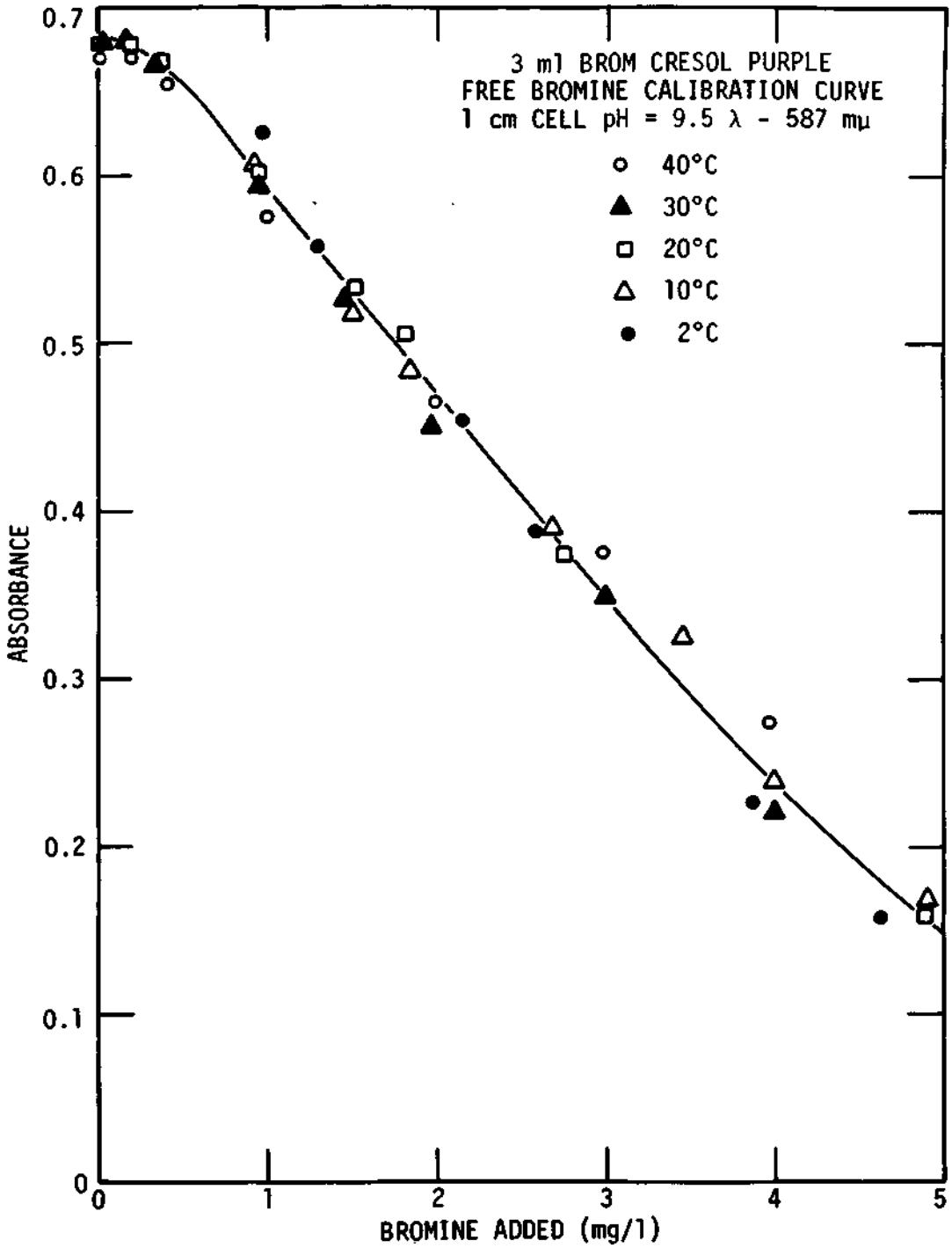

3 ml BROM CRESOL PURPLE
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 587 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
BROMINE ADDED (mg/l)

Figure 6

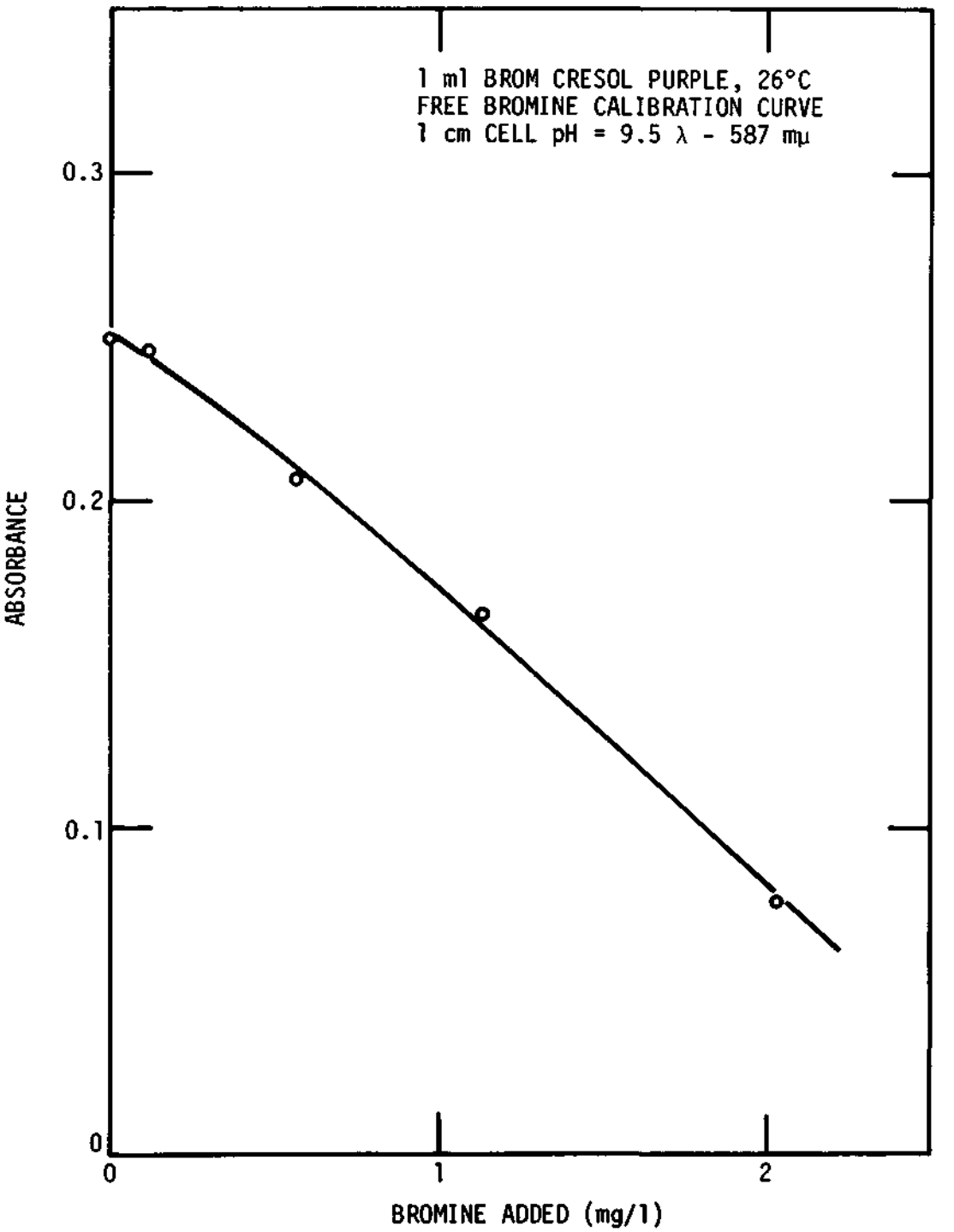

1 ml BROM CRESOL PURPLE, 26°C
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 587 mμ
ABSORBANCE
0.3
0.2
0.1
0
0
1
2
BROMINE ADDED (mg/l)

Figure 7

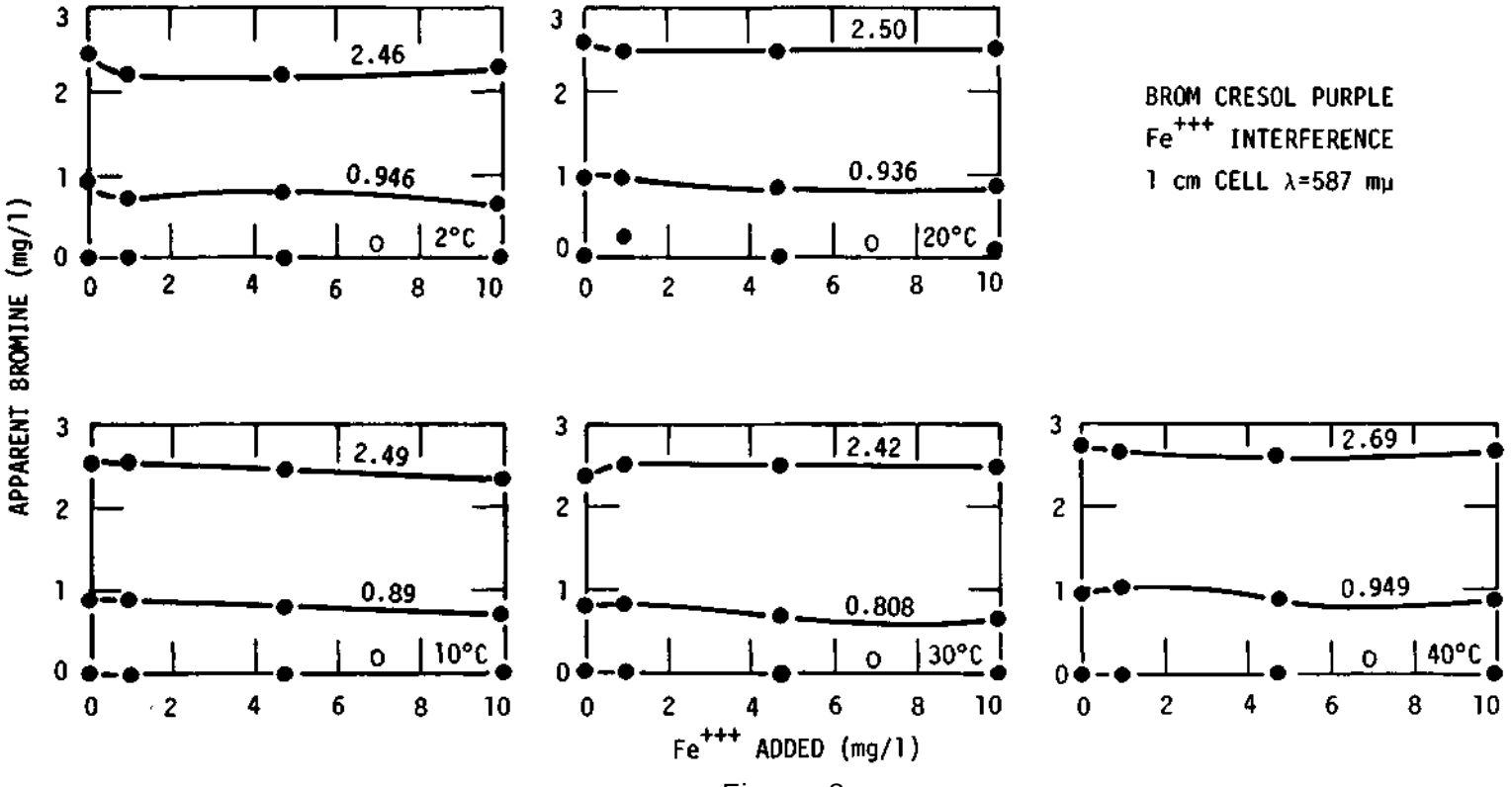

BROM CRESOL PURPLE
Fe+++ INTERFERENCE
1 cm CELL λ=587 mμ
APPARENT BROMINE (mg/l)
Fe+++ ADDED (mg/l)
2.46
0.946
2°C
2.50
0.936
20°C
2.49
0.89
10°C
2.42
0.808
30°C
2.69
0.949
40°C

Figure 8

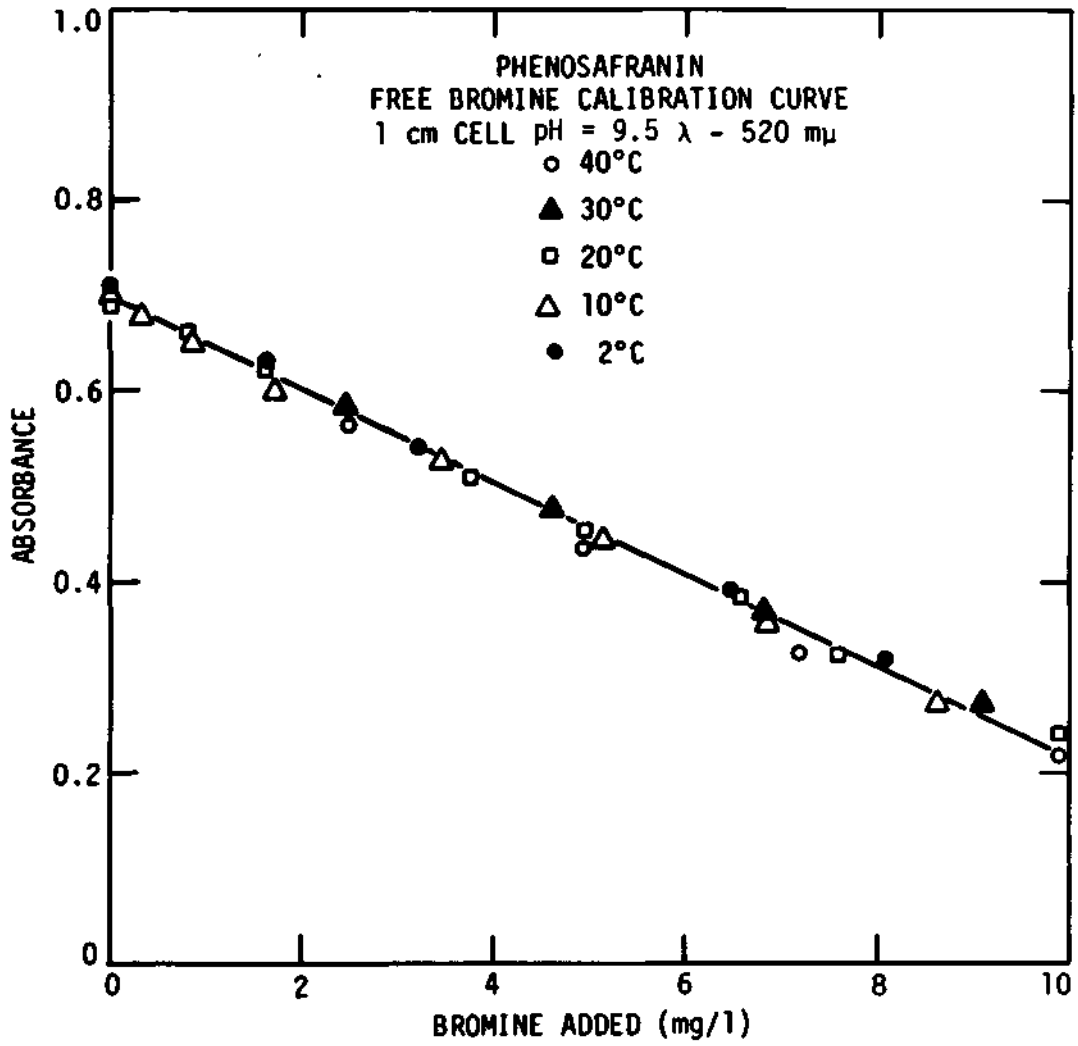

PHENOSAFRANIN
FREE BROMINE CALIBRATION CURVE
1 cm CELL pH = 9.5 λ - 520 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
BROMINE ADDED (mg/l)

Figure 9

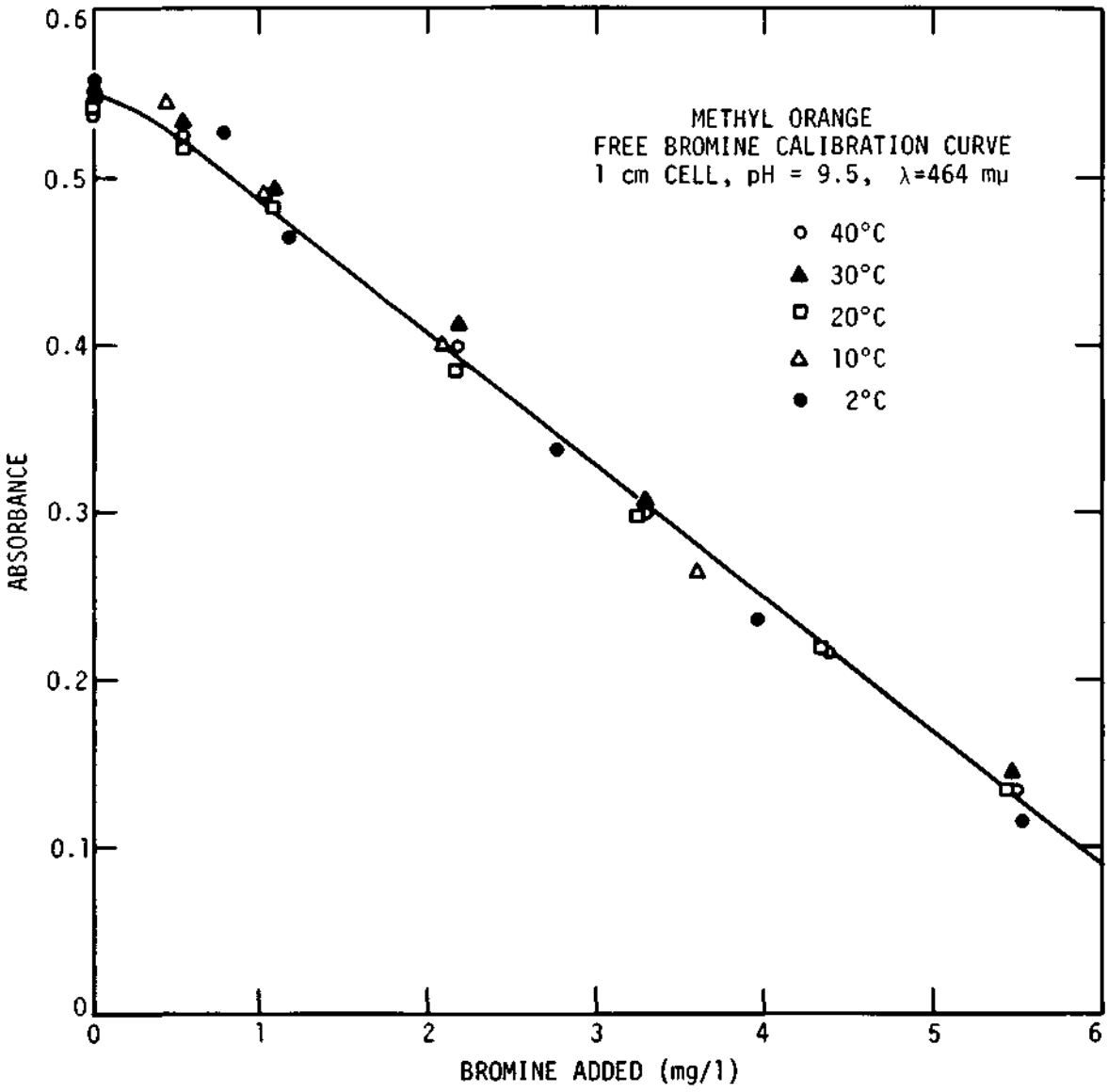

METHYL ORANGE
FREE BROMINE CALIBRATION CURVE
1 cm CELL, pH = 9.5, λ=464 mμ
40°C
30°C
20°C
10°C
2°C
ABSORBANCE
BROMINE ADDED (mg/l)
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3
4
5
6

Figure 10

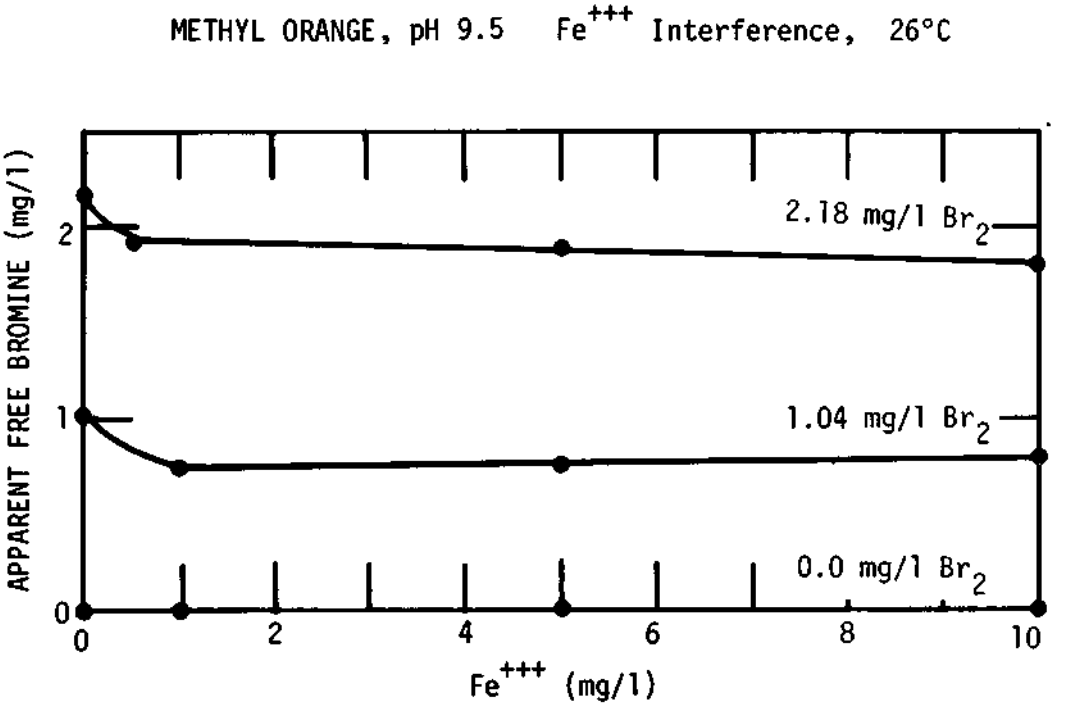

METHYL ORANGE, pH 9.5 Fe+++ Interference, 26°C
APPARENT FREE BROMINE (mg/l)
2.18 mg/l Br2
1.04 mg/l Br2
0.0 mg/l Br2
0
1
2
0
2
4
6
8
10
Fe+++ (mg/l)

Figure 11

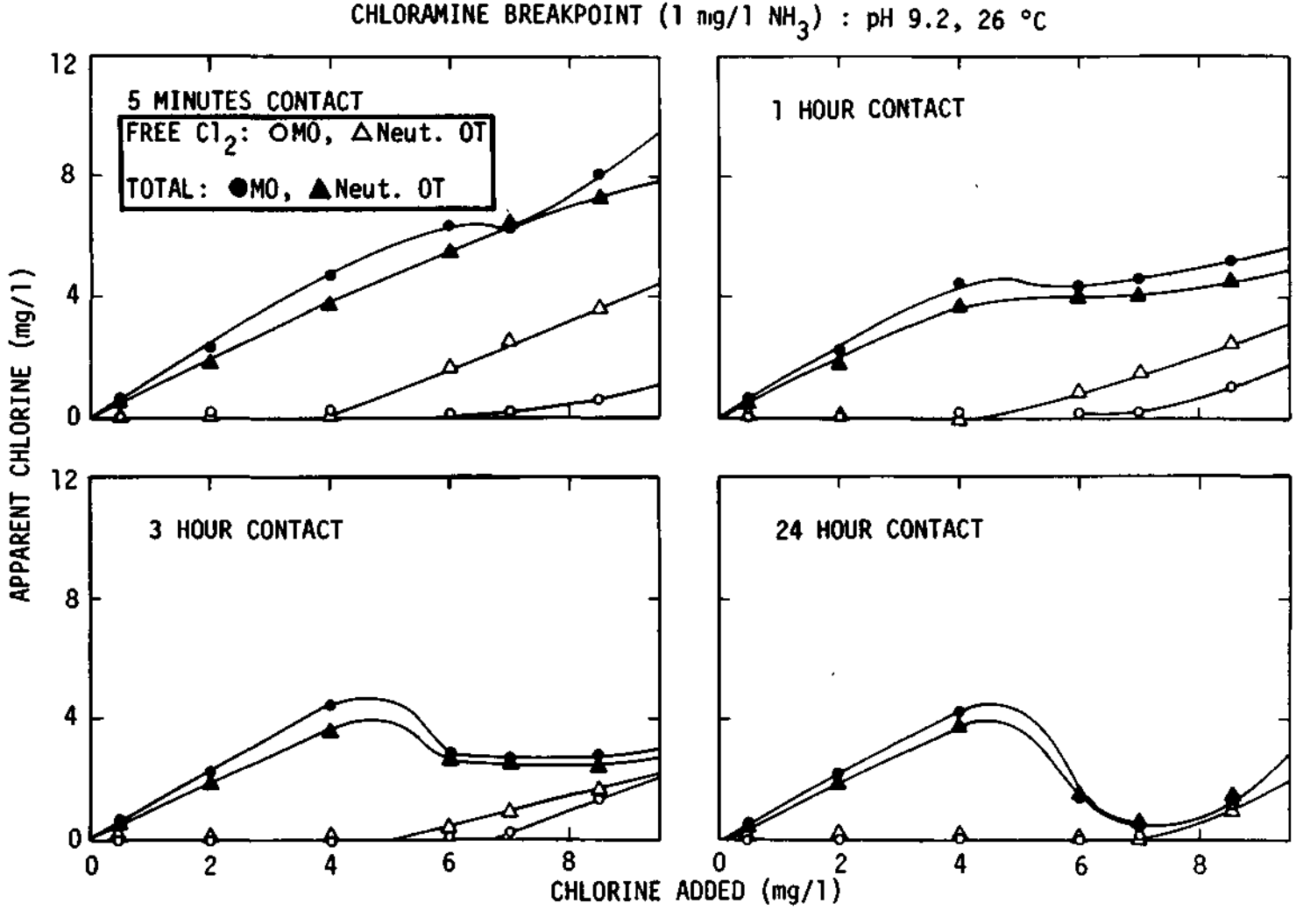

CHLORAMINE BREAKPOINT (1 mg/l NH_3) : pH 9.2, 26 °C
5 MINUTES CONTACT
FREE Cl_2: ○MO, △Neut. OT
TOTAL: ●MO, ▲Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
4
8
12
0
2
4
6
8

Figure 12

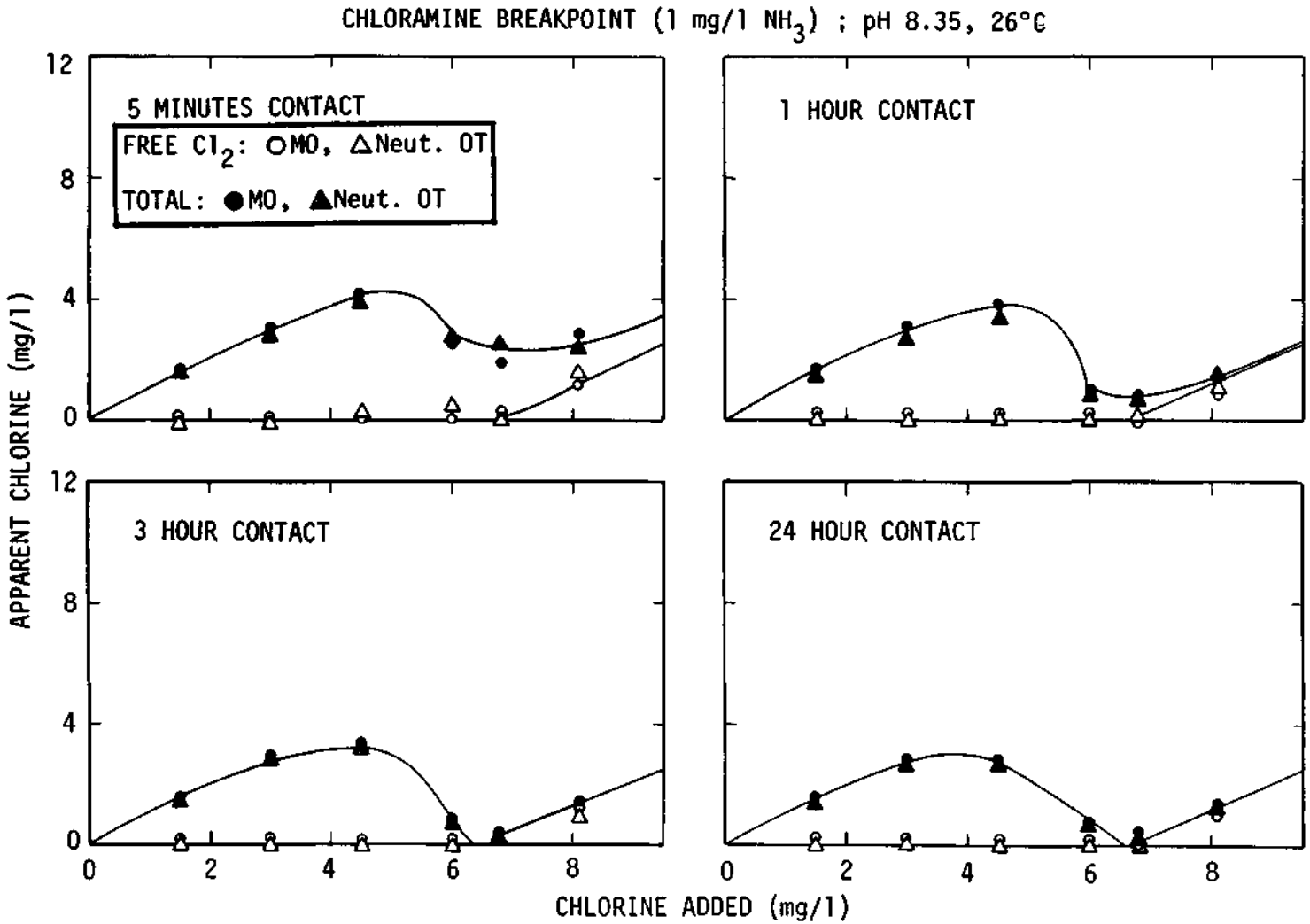

CHLORAMINE BREAKPOINT (1 mg/l NH_3) ; pH 8.35, 26°C
5 MINUTES CONTACT
FREE Cl_2: ○MO, △Neut. OT
TOTAL: ●MO, ▲Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2
4
6
8
12

Figure 13

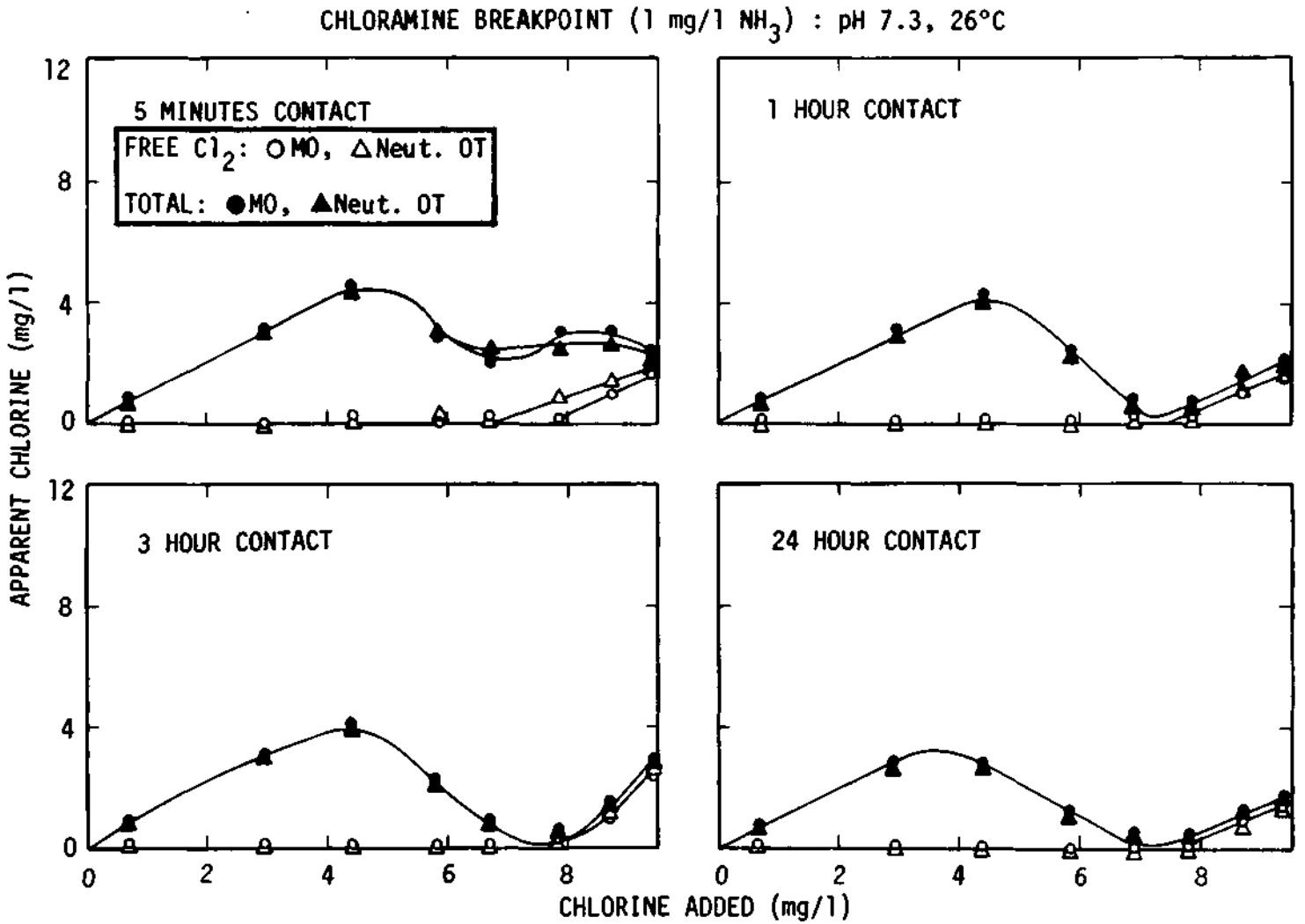

CHLORAMINE BREAKPOINT (1 mg/l NH_3) : pH 7.3, 26°C
5 MINUTES CONTACT
FREE Cl_2: ○MO, △Neut. OT
TOTAL: ●MO, ▲Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2
4
6
8
12

Figure 14

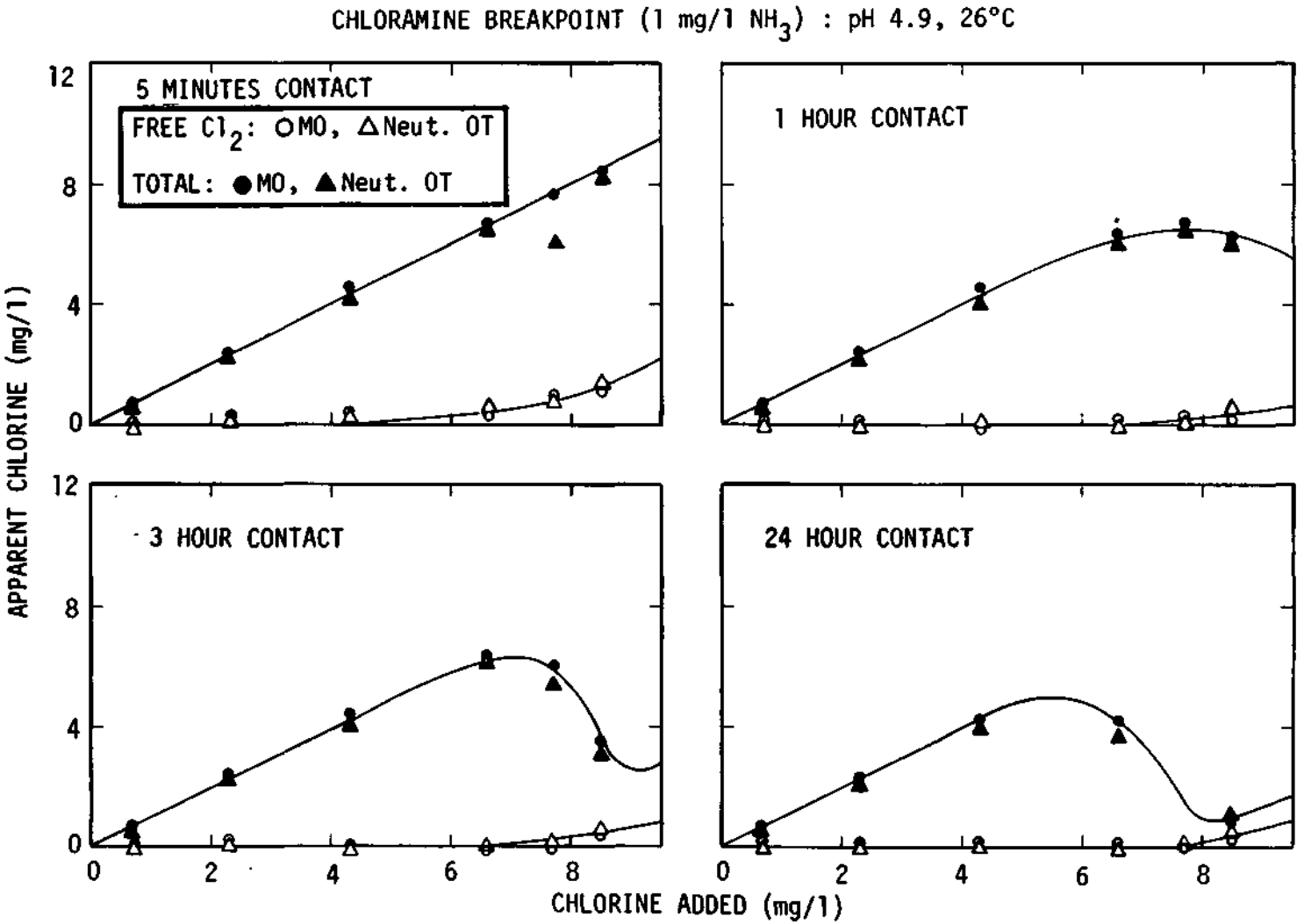

CHLORAMINE BREAKPOINT (1 mg/l NH_3) : pH 4.9, 26°C
5 MINUTES CONTACT
FREE Cl_2: ○MO, △Neut. OT
TOTAL: ●MO, ▲Neut. OT
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT CHLORINE (mg/l)
CHLORINE ADDED (mg/l)
0
2
4
6
8
12

Figure 15

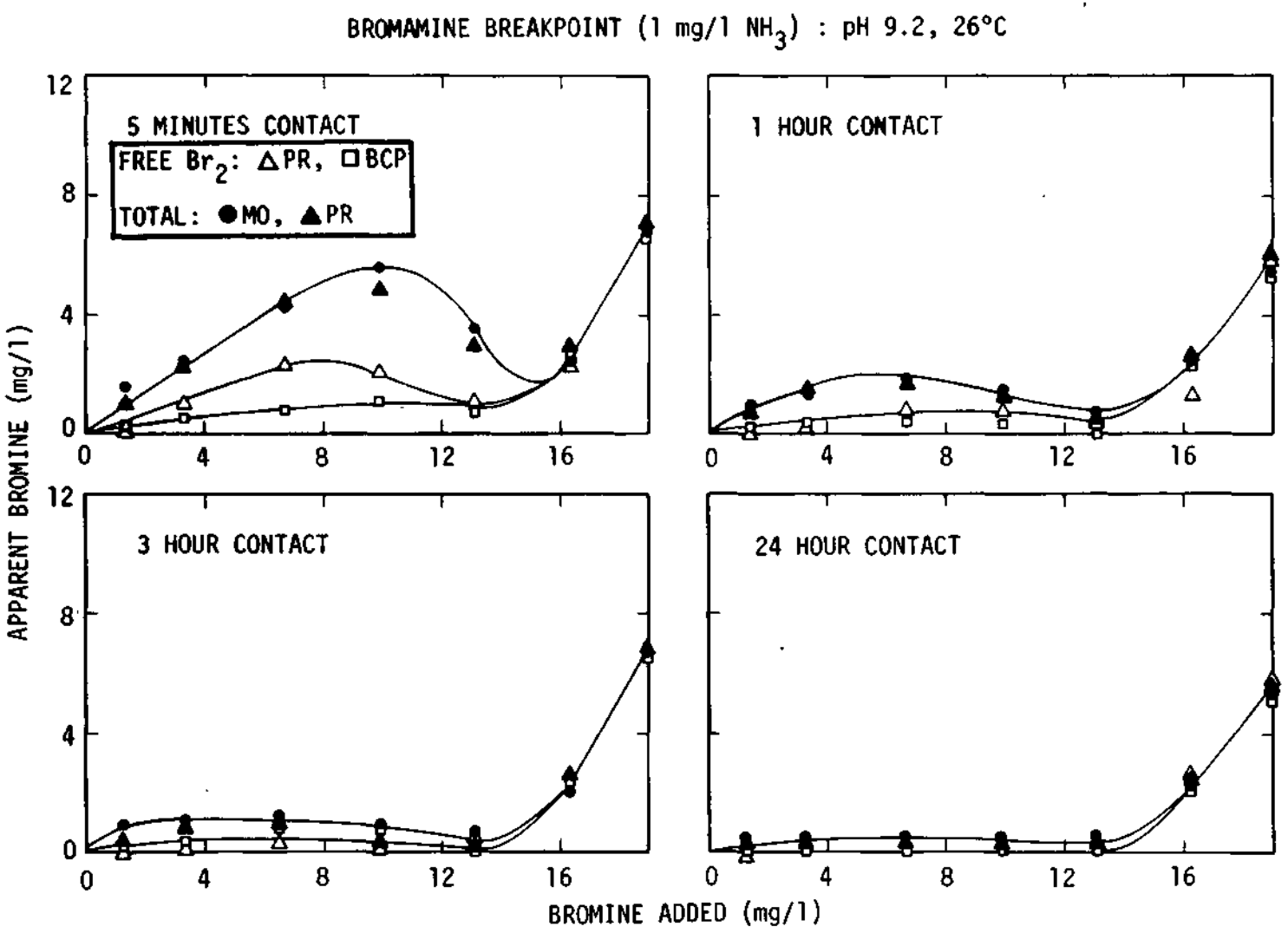

BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 9.2, 26°C
5 MINUTES CONTACT
FREE Br_2: △PR, □BCP
TOTAL: ●MO, ▲PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4
8
12
16

Figure 16

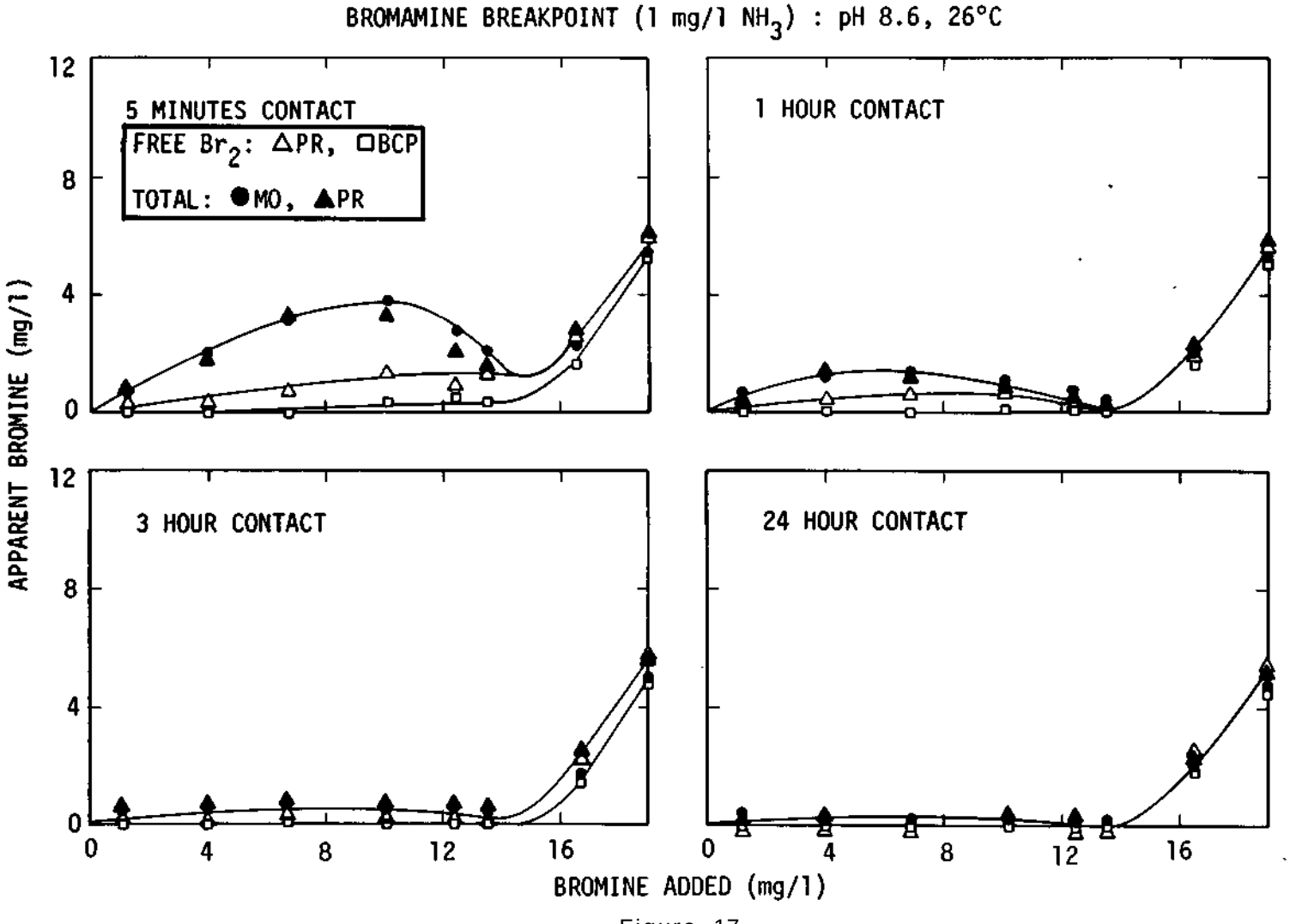

BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 8.6, 26°C
5 MINUTES CONTACT
FREE Br_2: △PR, □BCP
TOTAL: ●MO, ▲PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4
8
12
16

Figure 17

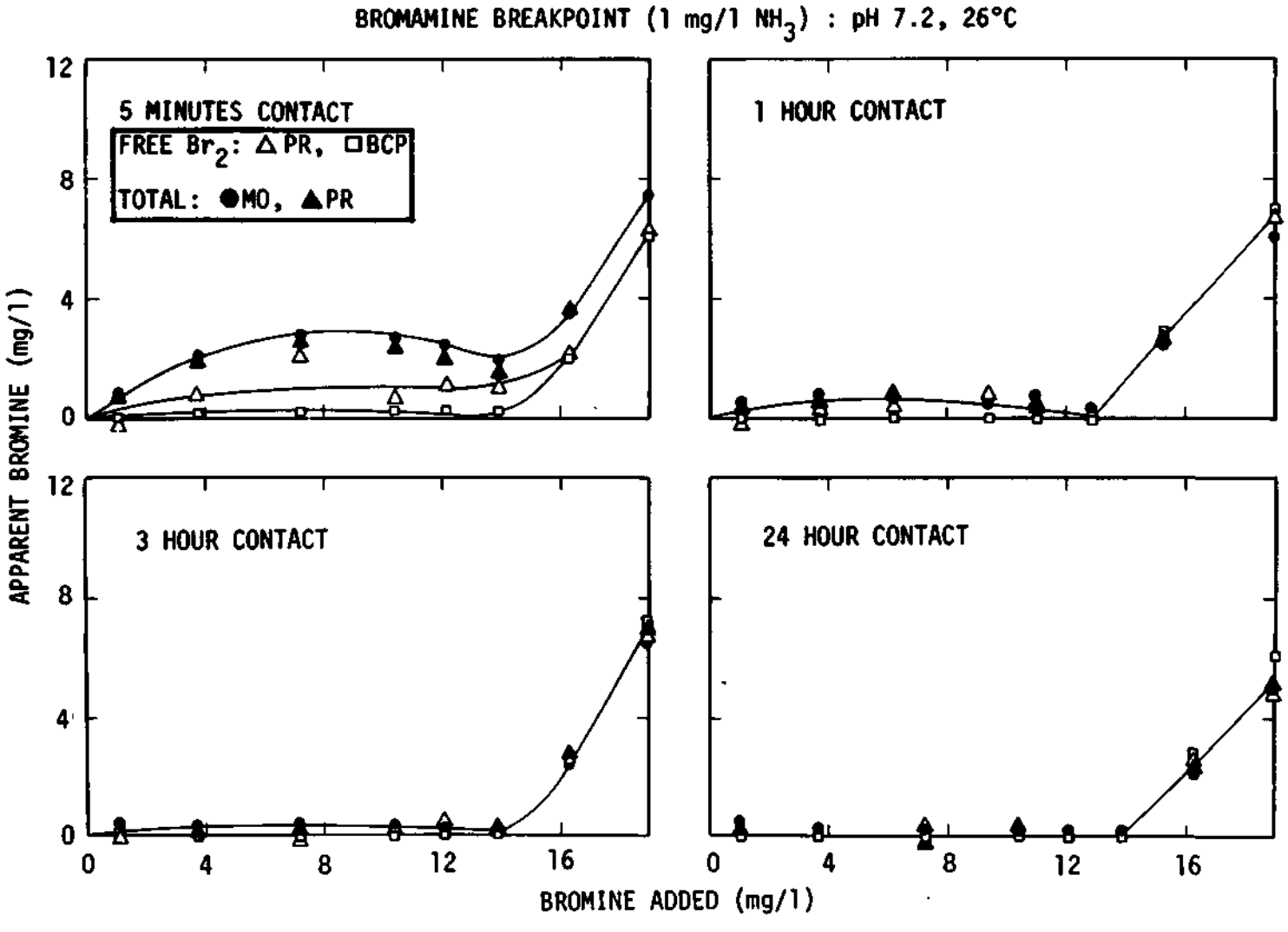

BROMAMINE BREAKPOINT (1 mg/l NH_3) : pH 7.2, 26°C
5 MINUTES CONTACT
FREE Br_2: △PR, □BCP
TOTAL: ●MO, ▲PR
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
0
4
8
12
16

Figure 18

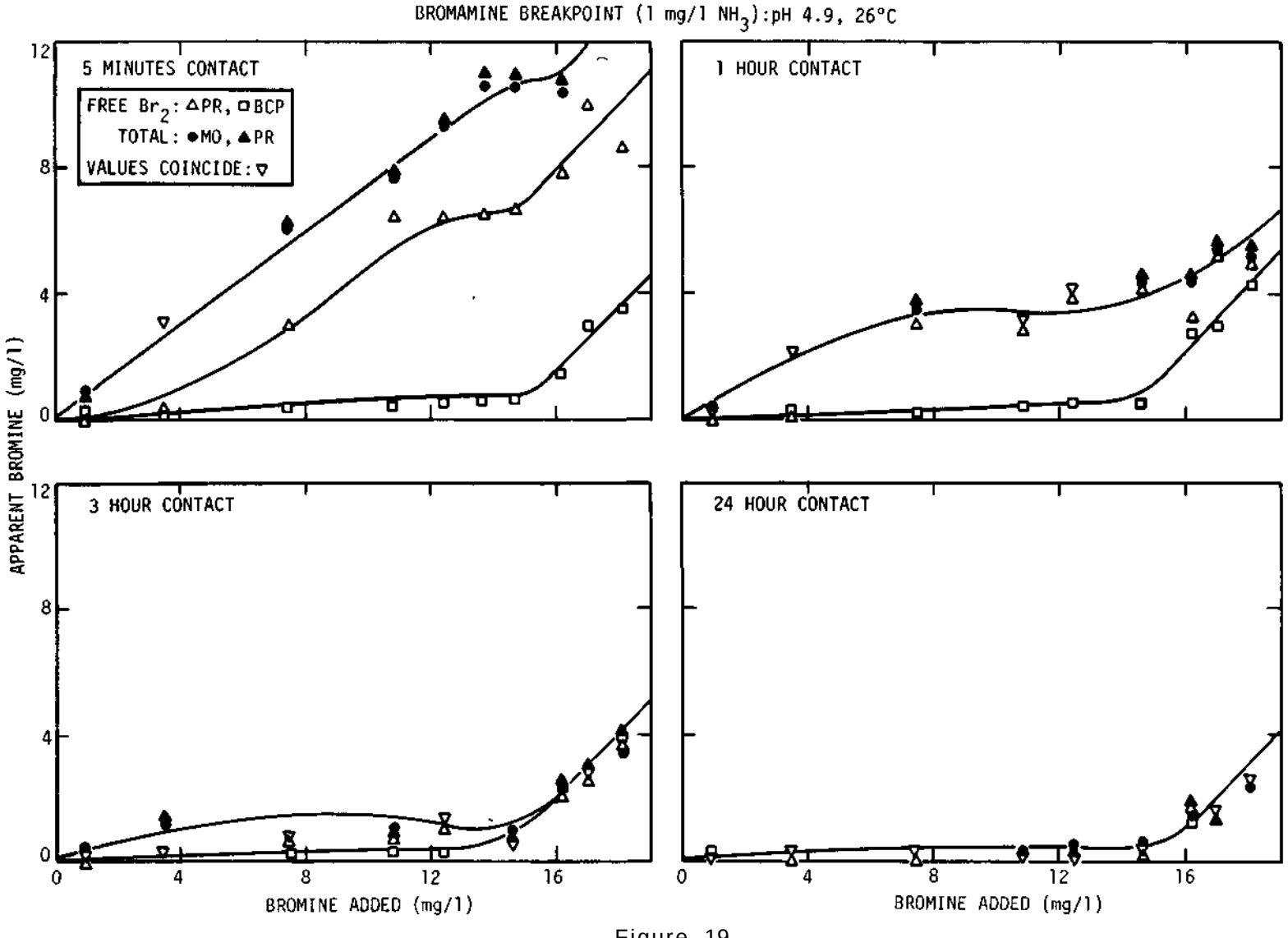

BROMAMINE BREAKPOINT (1 mg/l NH_3):pH 4.9, 26°C
5 MINUTES CONTACT
FREE Br_2: △PR, □BCP
TOTAL: ●MO, ▲PR
VALUES COINCIDE: ▽
1 HOUR CONTACT
3 HOUR CONTACT
24 HOUR CONTACT
APPARENT BROMINE (mg/l)
BROMINE ADDED (mg/l)
BROMINE ADDED (mg/l)
0
4
8
12
16

Figure 19

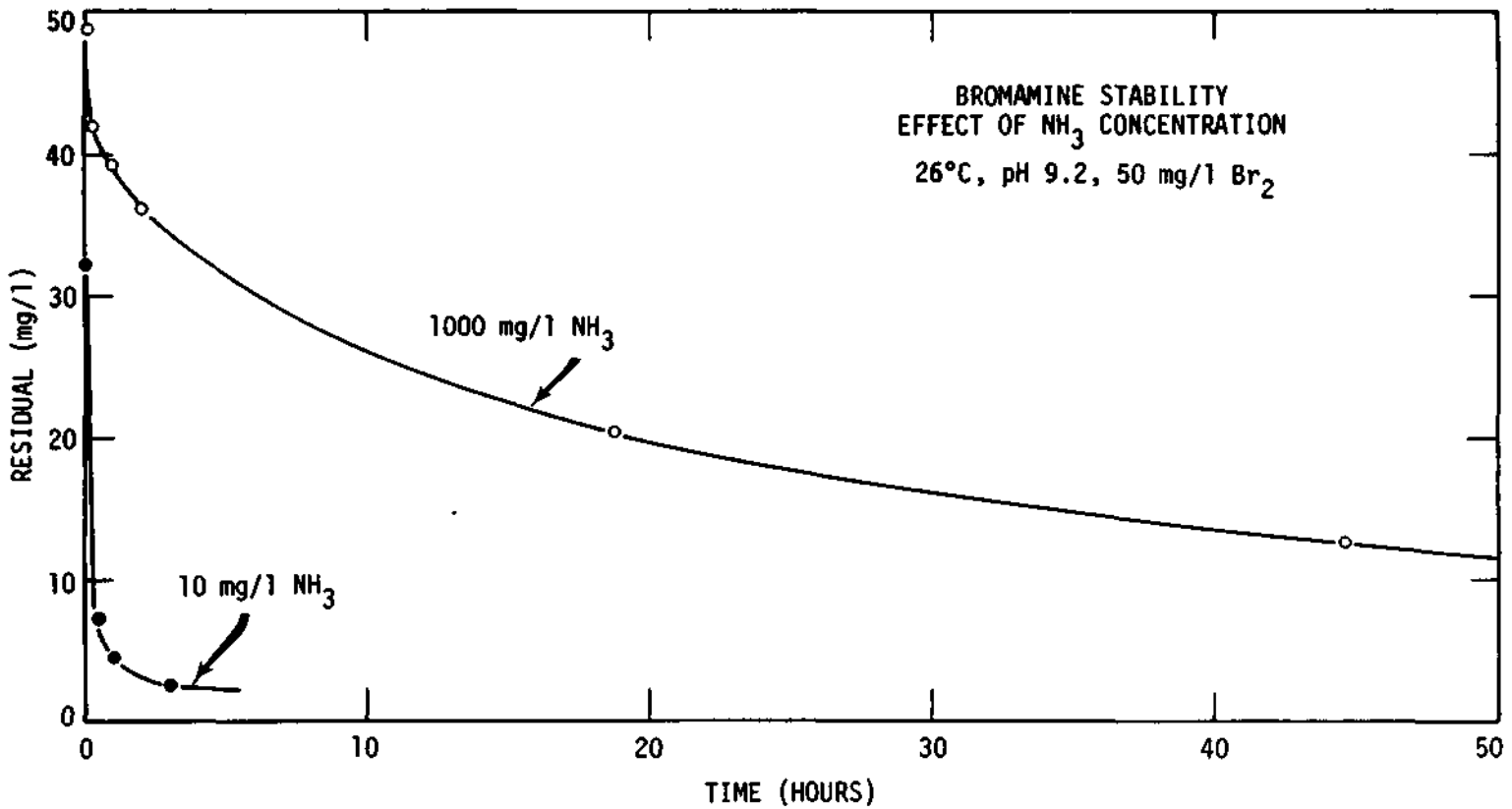

BROMAMINE STABILITY
EFFECT OF NH_3 CONCENTRATION
26°C, pH 9.2, 50 mg/l Br_2
1000 mg/l NH_3
10 mg/l NH_3
RESIDUAL (mg/l)
TIME (HOURS)
0
10
20
30
40
50

Figure 20

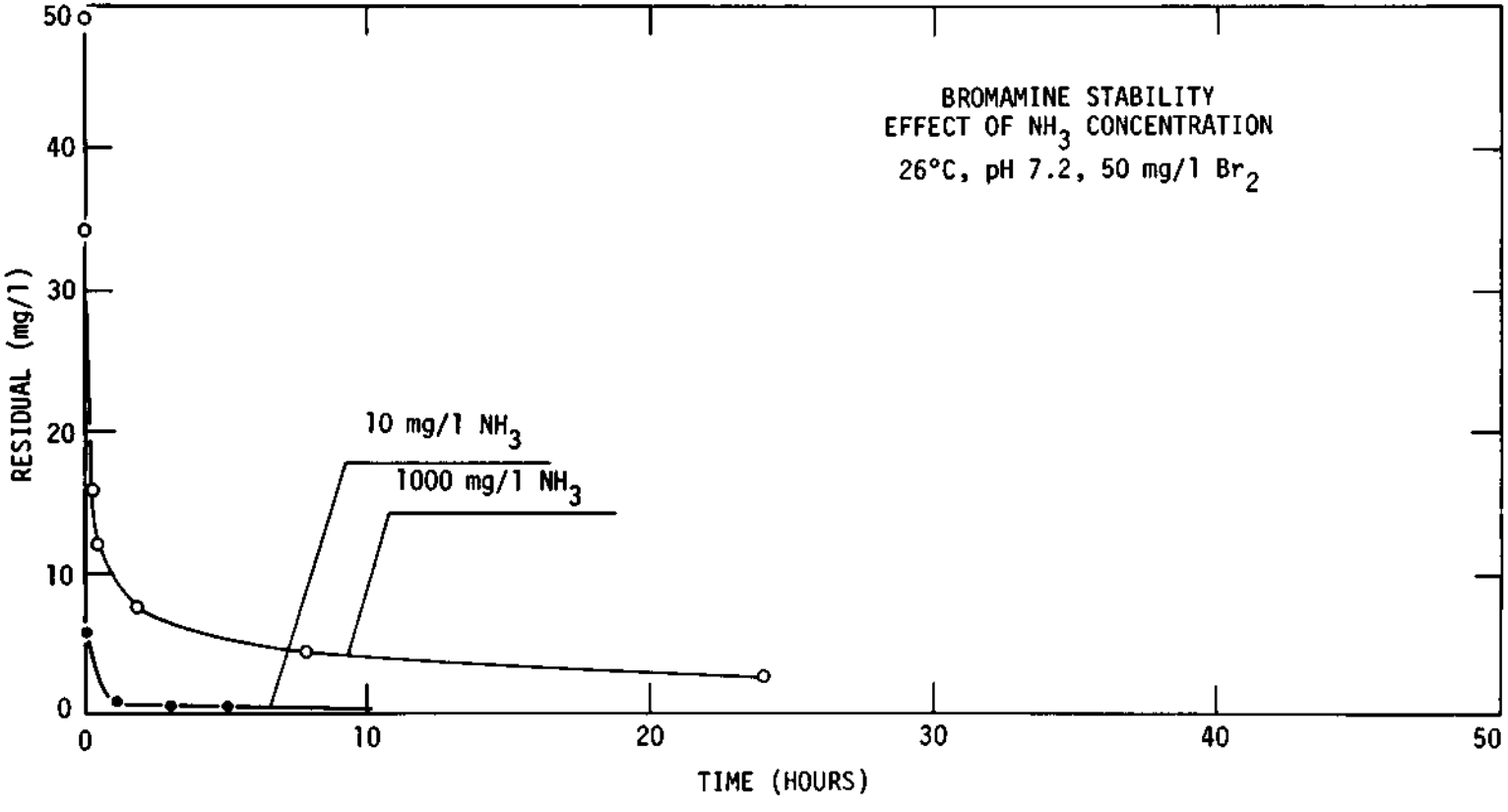

BROMAMINE STABILITY
EFFECT OF NH_3 CONCENTRATION
26°C, pH 7.2, 50 mg/l Br_2
10 mg/l NH_3
1000 mg/l NH_3
RESIDUAL (mg/l)
TIME (HOURS)
0
10
20
30
40
50

Figure 21

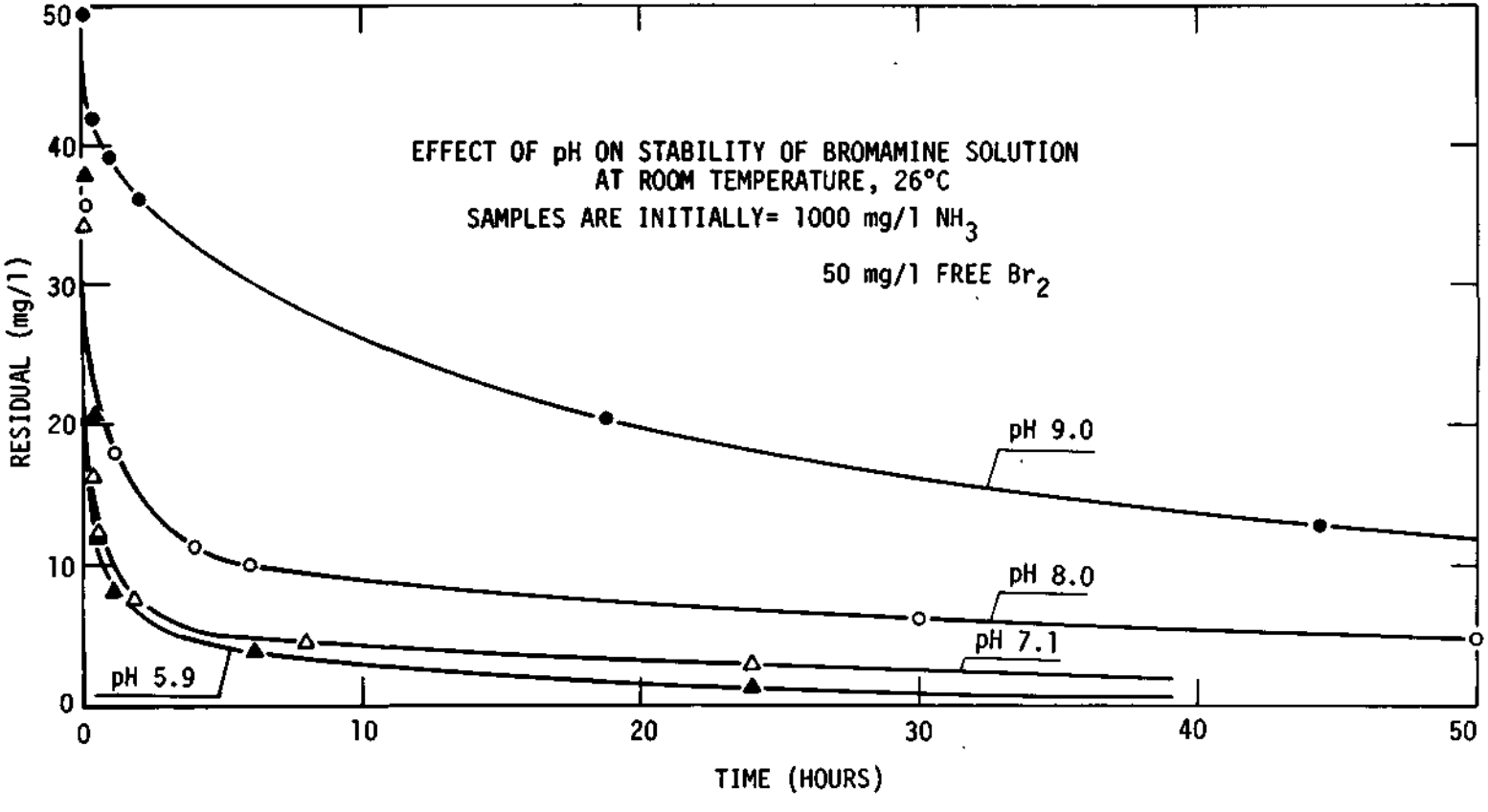

EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE, 26°C
SAMPLES ARE INITIALLY= 1000 mg/l NH_3
50 mg/l FREE Br_2
pH 9.0
pH 8.0
pH 7.1
pH 5.9
RESIDUAL (mg/l)
TIME (HOURS)
0
10
20
30
40
50

Figure 22

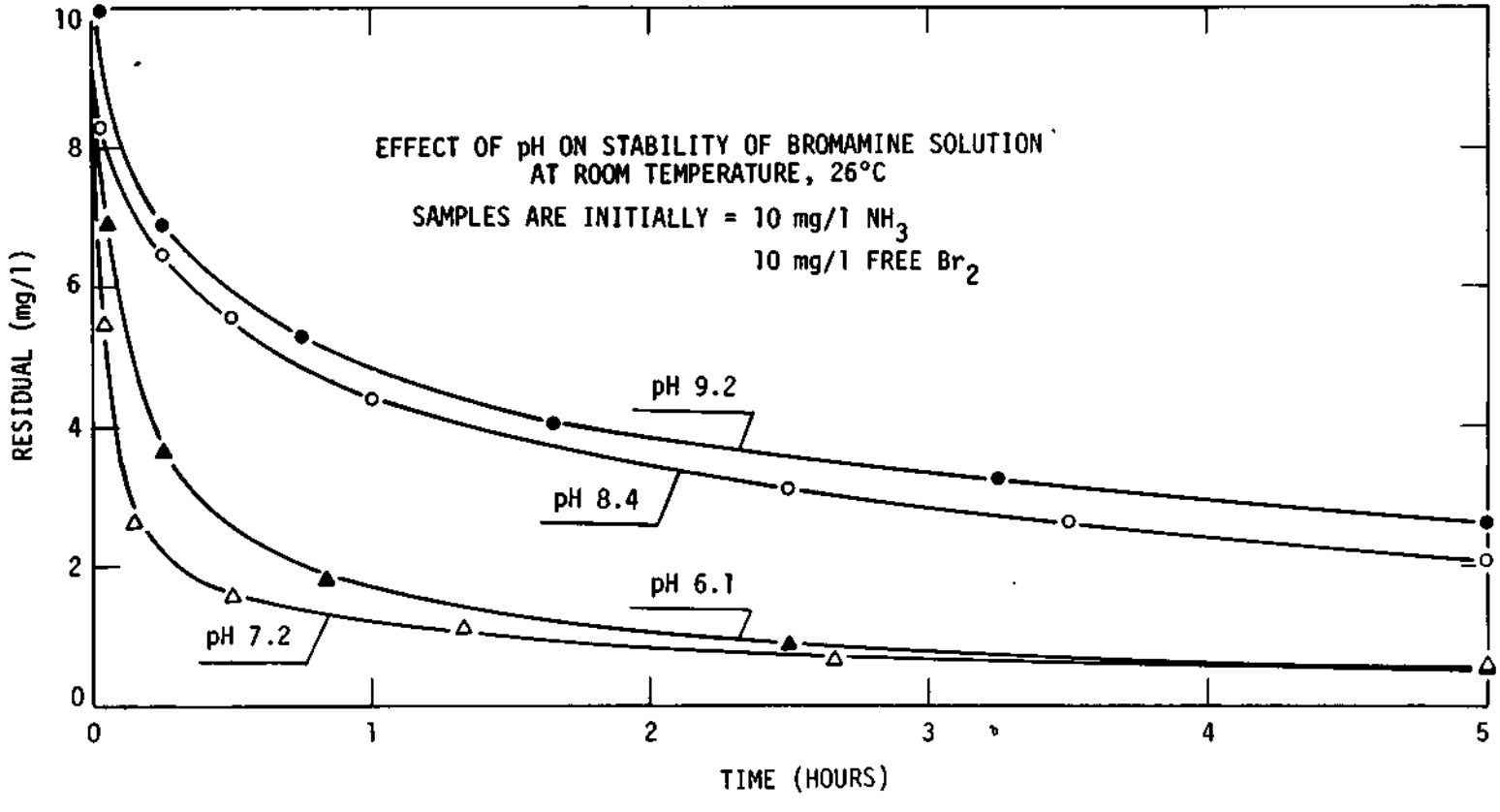

EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE, 26°C
SAMPLES ARE INITIALLY = 10 mg/l NH_3
10 mg/l FREE Br_2
pH 9.2
pH 8.4
pH 6.1
pH 7.2
RESIDUAL (mg/l)
TIME (HOURS)
0
2
4
6
8
10
0
1
2
3
4
5

Figure 23

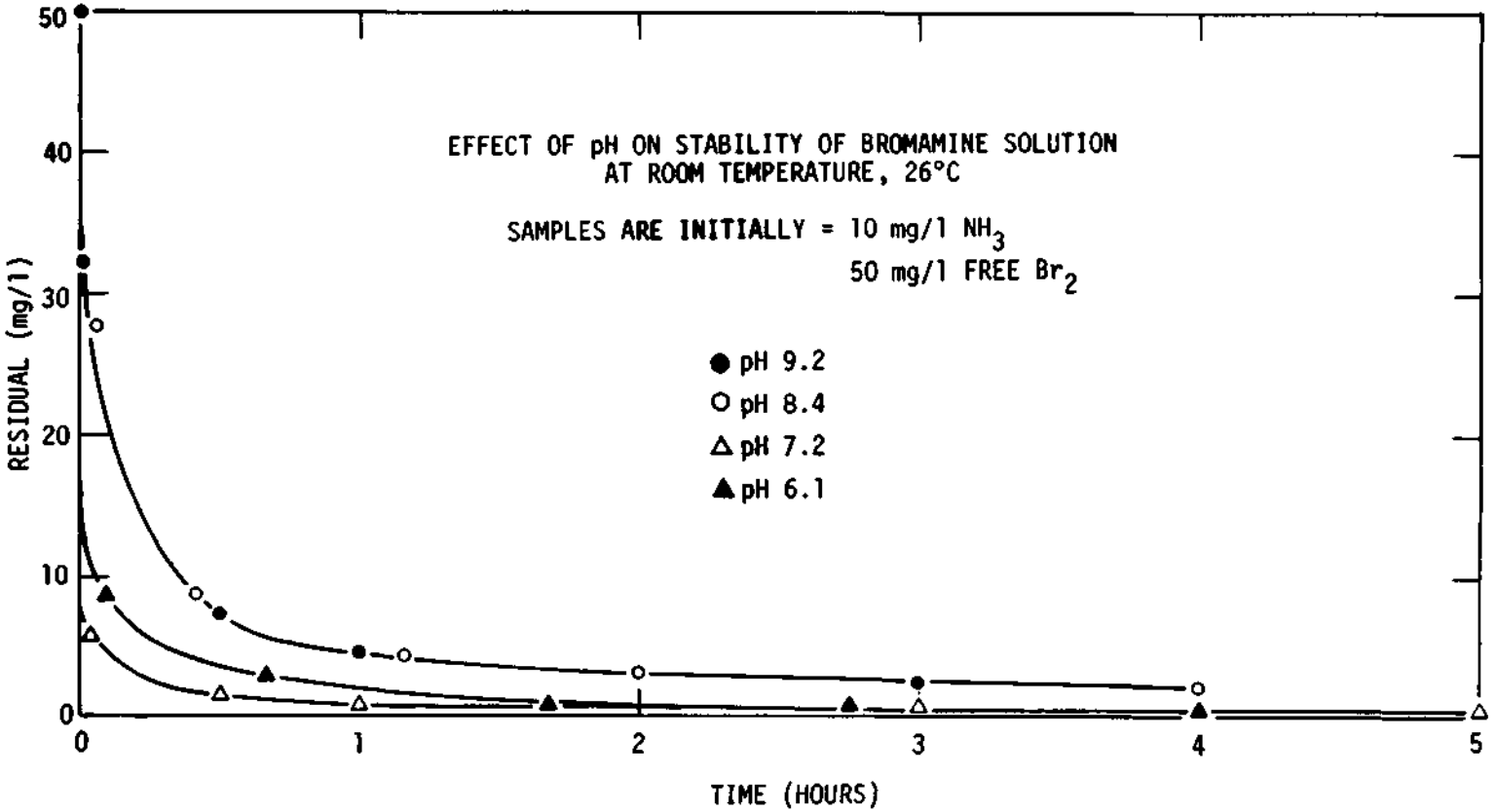

EFFECT OF pH ON STABILITY OF BROMAMINE SOLUTION
AT ROOM TEMPERATURE, 26°C
SAMPLES ARE INITIALLY = 10 mg/l NH_3
50 mg/l FREE Br_2
● pH 9.2
○ pH 8.4
△ pH 7.2
▲ pH 6.1
RESIDUAL (mg/l)
TIME (HOURS)
0
10
20
30
40
50
0
1
2
3
4
5

Figure 24

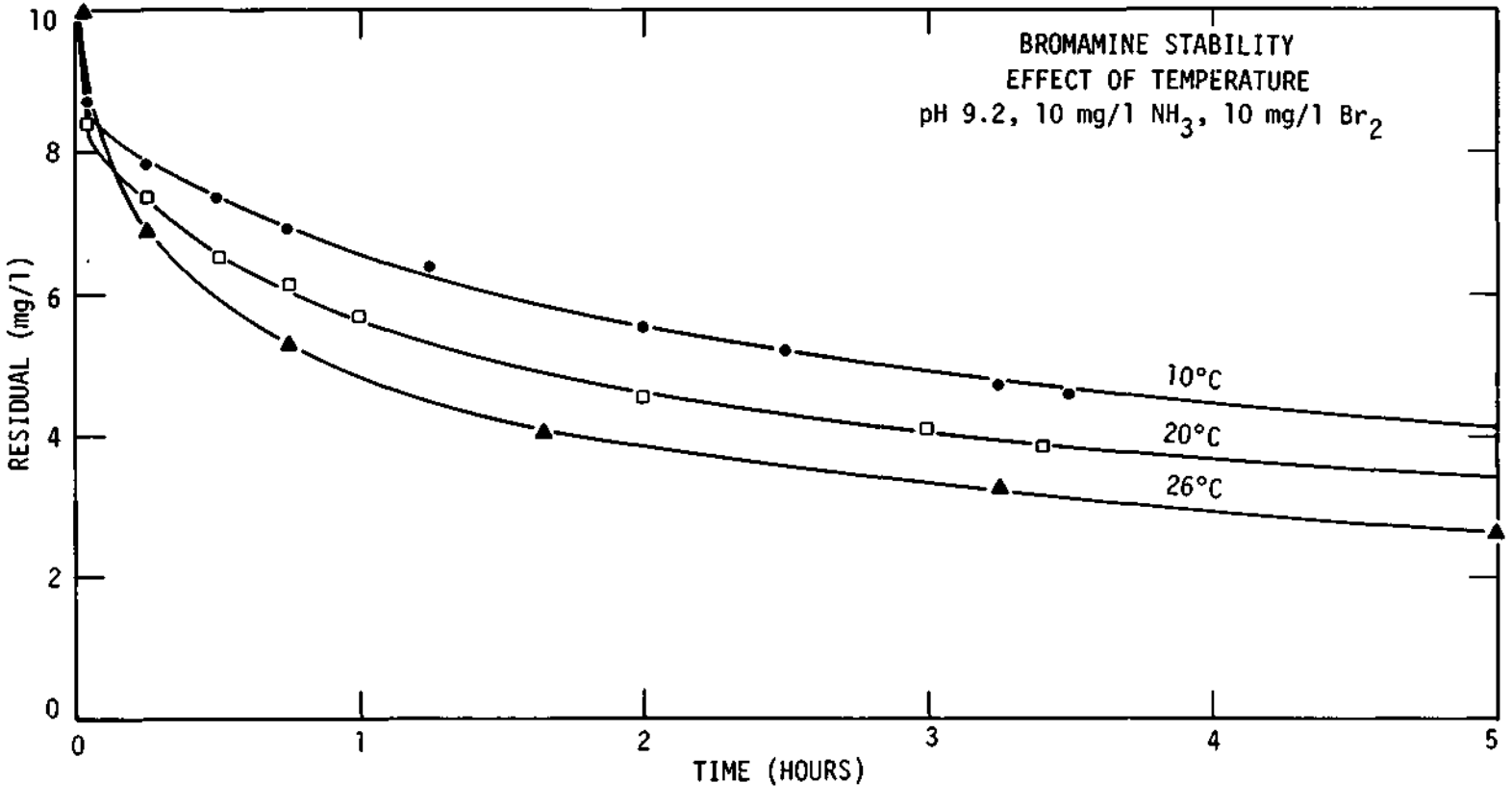

BROMAMINE STABILITY
EFFECT OF TEMPERATURE
pH 9.2, 10 mg/l NH_3, 10 mg/l Br_2
10°C
20°C
26°C
RESIDUAL (mg/l)
TIME (HOURS)
0
2
4
6
8
10
0
1
2
3
4
5

Figure 25

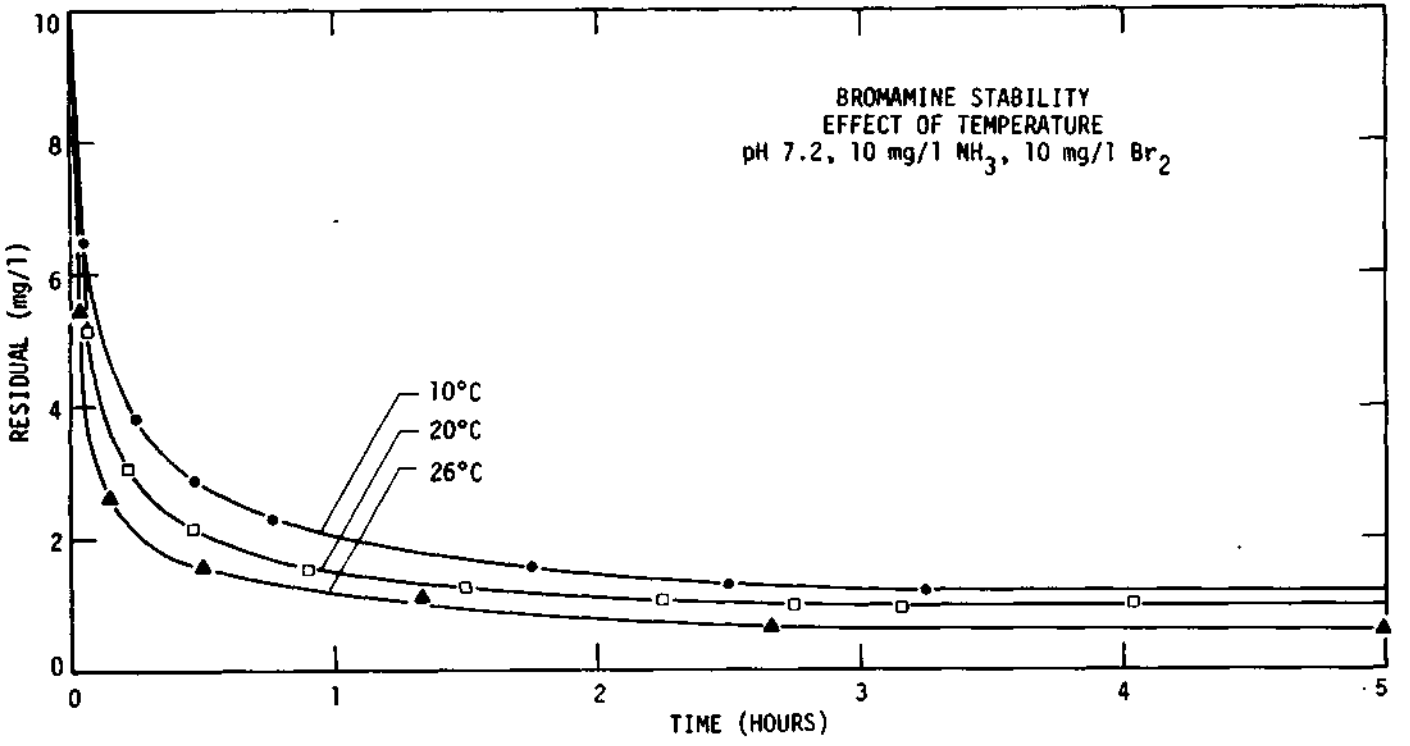

BROMAMINE STABILITY
EFFECT OF TEMPERATURE
pH 7.2, 10 mg/l NH_3, 10 mg/l Br_2
10°C
20°C
26°C
RESIDUAL (mg/l)
TIME (HOURS)
0
2
4
6
8
10
0
1
2
3
4
5

Figure 26

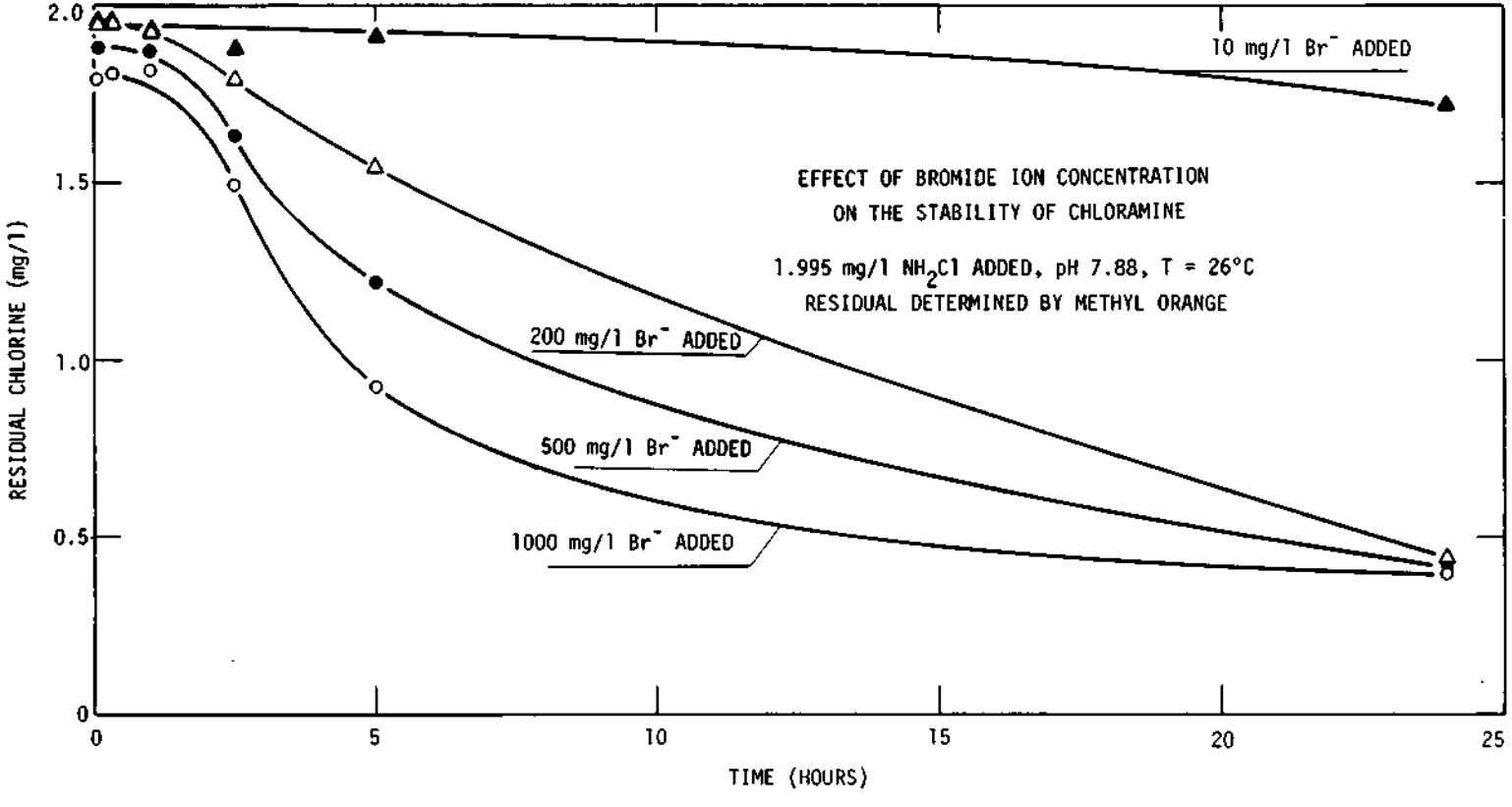

EFFECT OF BROMIDE ION CONCENTRATION
ON THE STABILITY OF CHLORAMINE
1.995 mg/l NH2Cl ADDED, pH 7.88, T = 26°C
RESIDUAL DETERMINED BY METHYL ORANGE
10 mg/l Br⁻ ADDED
200 mg/l Br⁻ ADDED
500 mg/l Br⁻ ADDED
1000 mg/l Br⁻ ADDED
RESIDUAL CHLORINE (mg/l)
TIME (HOURS)
2.0
1.5
1.0
0.5
0
0
5
10
15
20
25

Figure 27

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

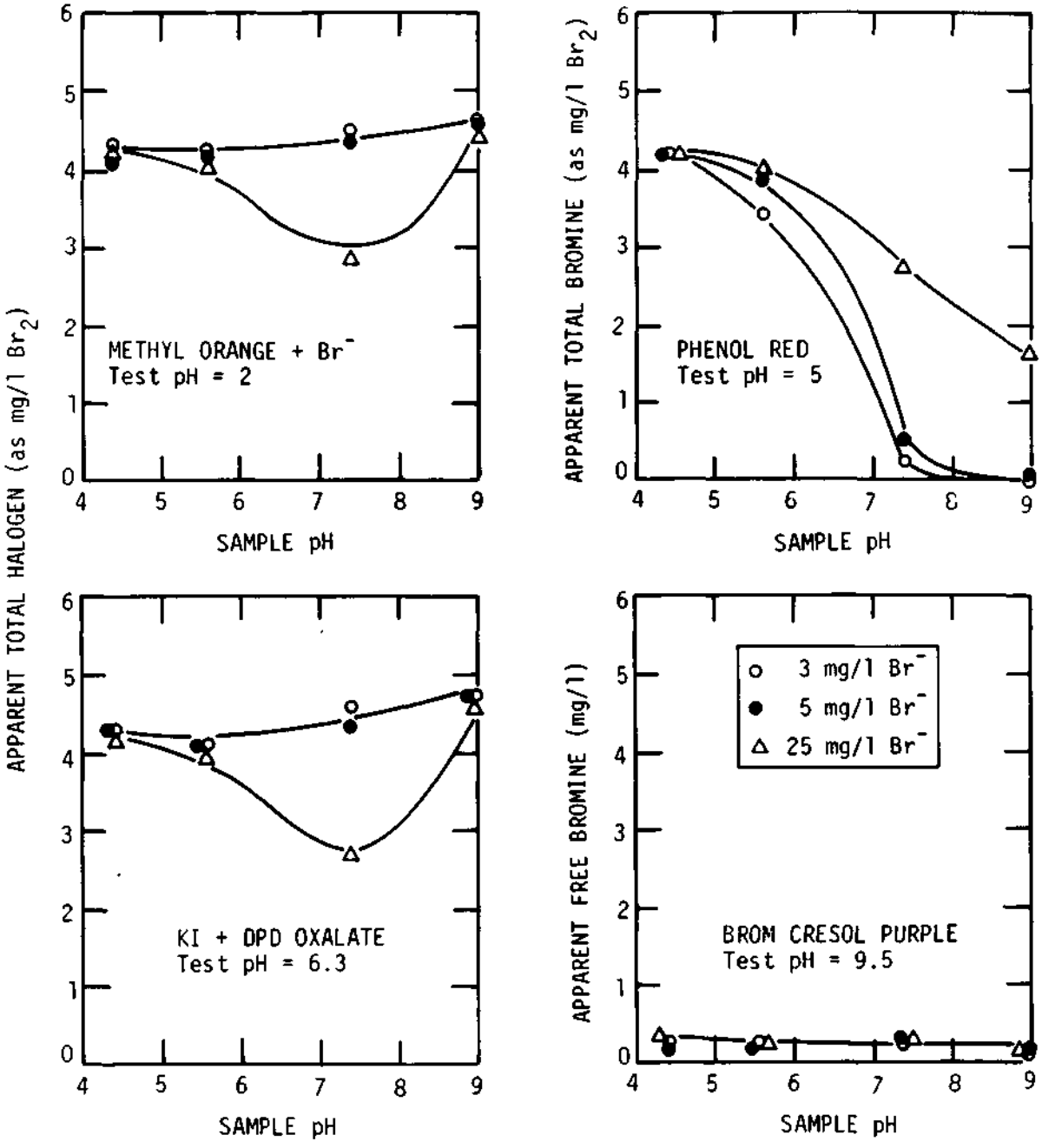


Figure 28

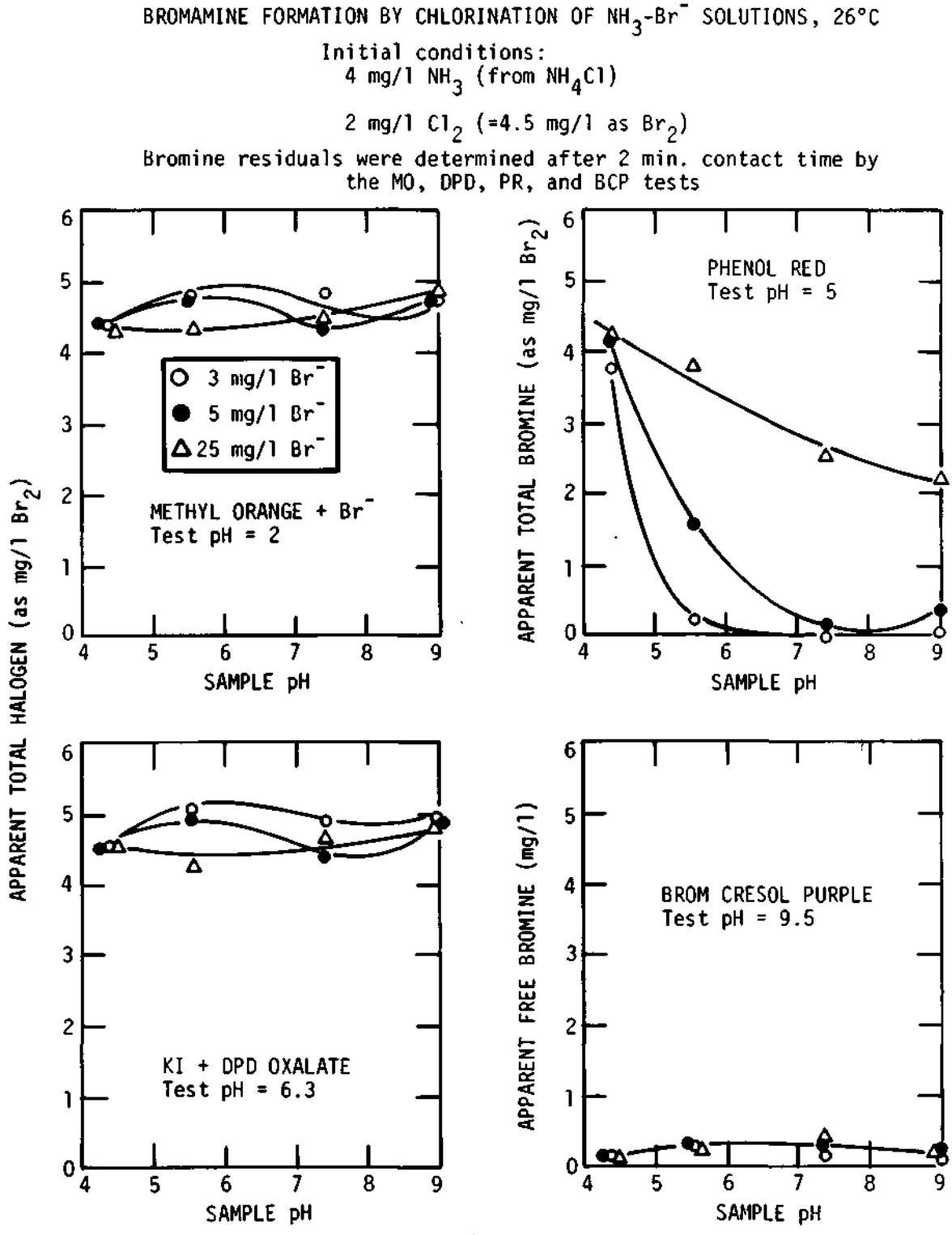

BROMAMINE FORMATION BY CHLORINATION OF NH_3-Br^- SOLUTIONS, 26°C
Initial conditions:
4 mg/l NH_3 (from NH_4Cl)
2 mg/l Cl_2 (=4.5 mg/l as Br_2)
Bromine residuals were determined after 2 min. contact time by the MO, DPD, PR, and BCP tests
APPARENT TOTAL HALOGEN (as mg/l Br_2)
3 mg/l Br^-
5 mg/l Br^-
25 mg/l Br^-
METHYL ORANGE + Br^-
Test pH = 2
SAMPLE pH
APPARENT TOTAL BROMINE (as mg/l Br_2)
PHENOL RED
Test pH = 5
SAMPLE pH
KI + DPD OXALATE
Test pH = 6.3
SAMPLE pH
APPARENT FREE BROMINE (mg/l)
BROM CRESOL PURPLE
Test pH = 9.5
SAMPLE pH

Figure 29

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

Initial conditions:
0.5 mg/l NH_3 (from NH_4Cl)
3 mg/l Cl_2 (=6.75 mg/l as Br_2)
Bromine residuals were determined after 5 min. contact time by the MO, DPD, PR, and BCP tests

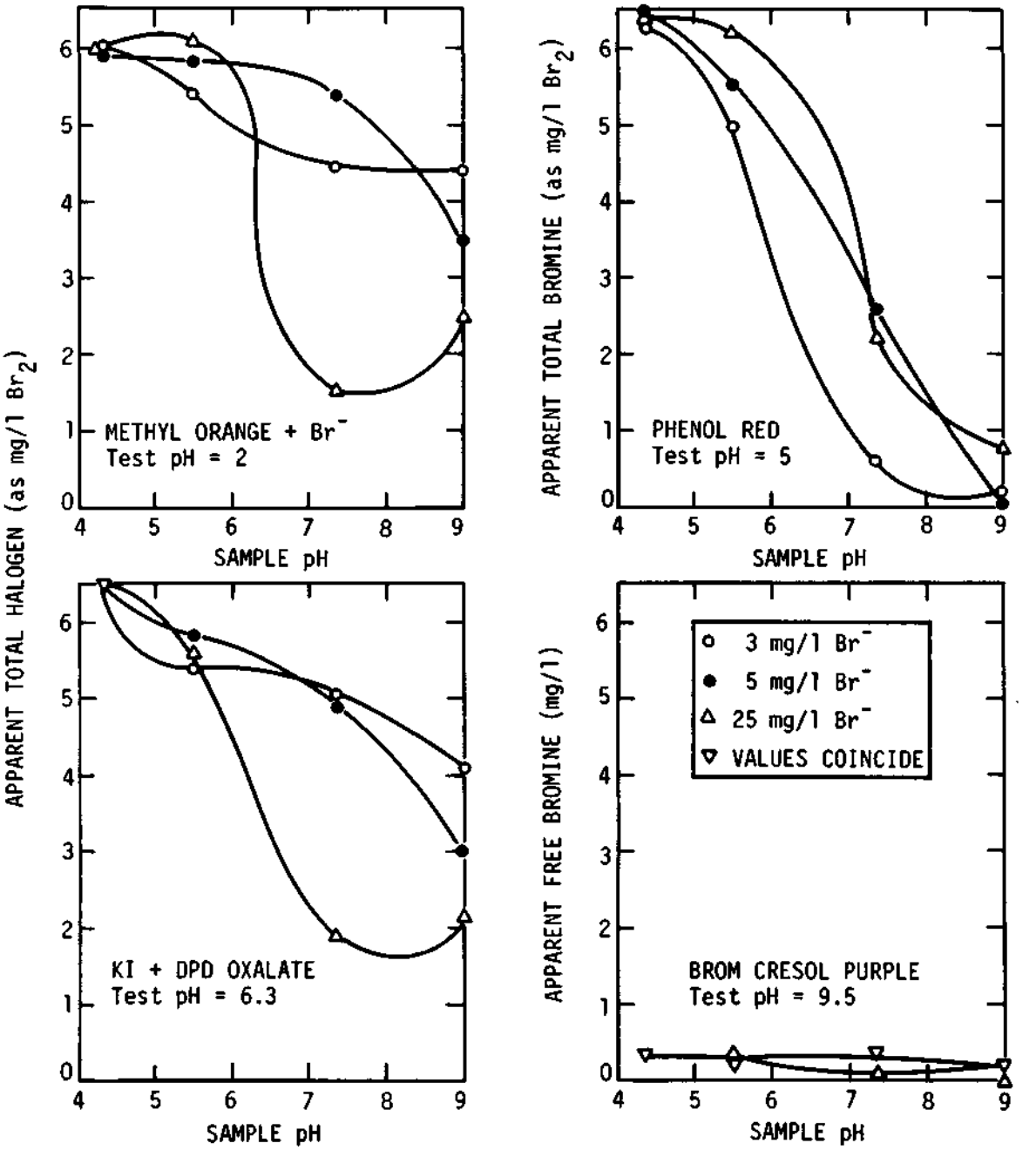


Figure 30

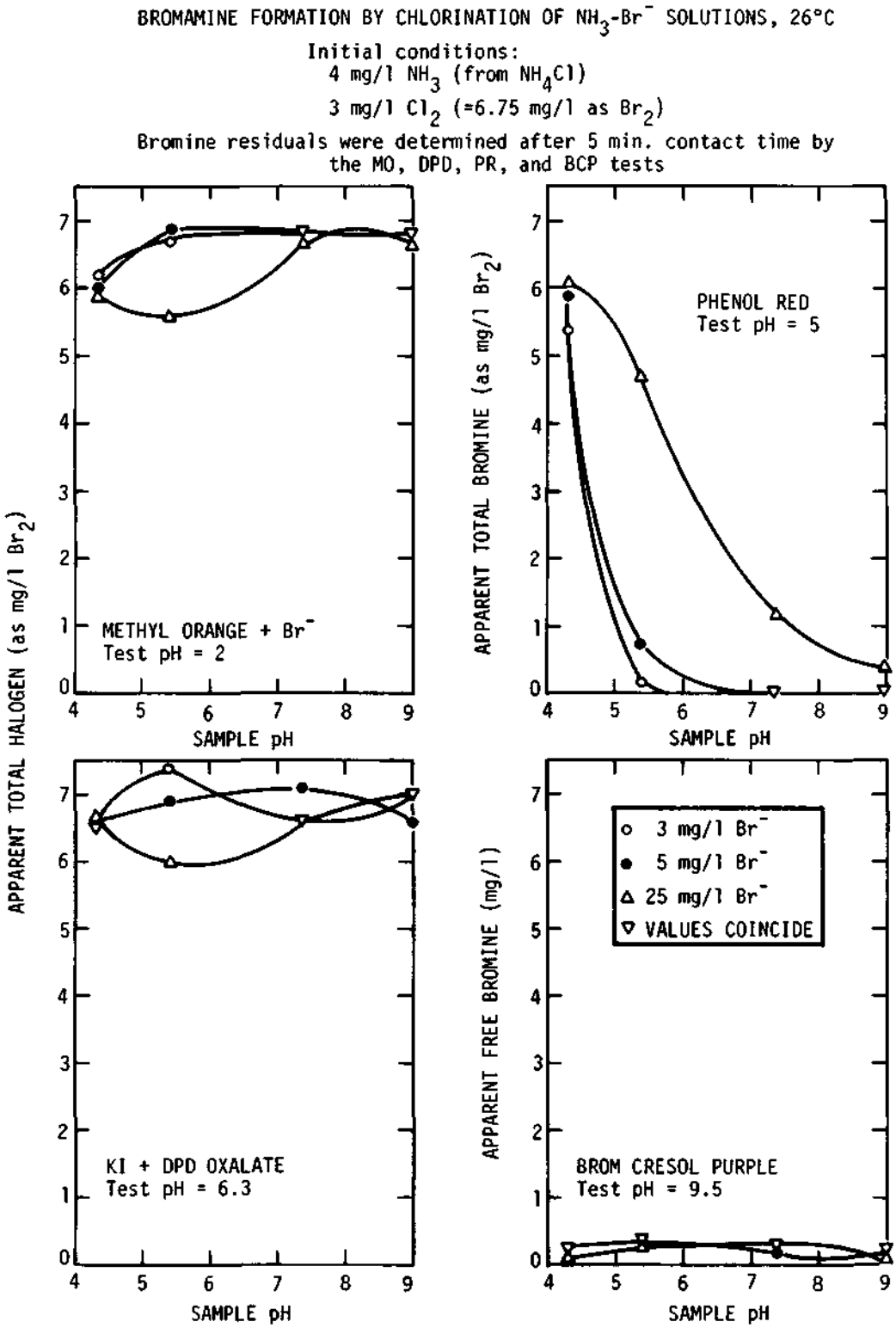

BROMAMINE FORMATION BY CHLORINATION OF NH_3-Br^- SOLUTIONS, 26°C
Initial conditions:
4 mg/l NH_3 (from NH_4Cl)
3 mg/l Cl_2 (=6.75 mg/l as Br_2)
Bromine residuals were determined after 5 min. contact time by the MO, DPD, PR, and BCP tests
APPARENT TOTAL HALOGEN (as mg/l Br_2)
METHYL ORANGE + Br^-
Test pH = 2
APPARENT TOTAL BROMINE (as mg/l Br_2)
PHENOL RED
Test pH = 5
KI + DPD OXALATE
Test pH = 6.3
APPARENT FREE BROMINE (mg/l)
BROM CRESOL PURPLE
Test pH = 9.5
3 mg/l Br^-
5 mg/l Br^-
25 mg/l Br^-
VALUES COINCIDE
SAMPLE pH

Figure 31

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

Initial conditions:
0.5 mg/l NH_3 (from NH_4Cl)
2 mg/l Cl_2 (=4.5 mg/l as Br_2)

Bromine residuals were determined after 10 min. contact time by the MO, DPD, PR, and BCP tests

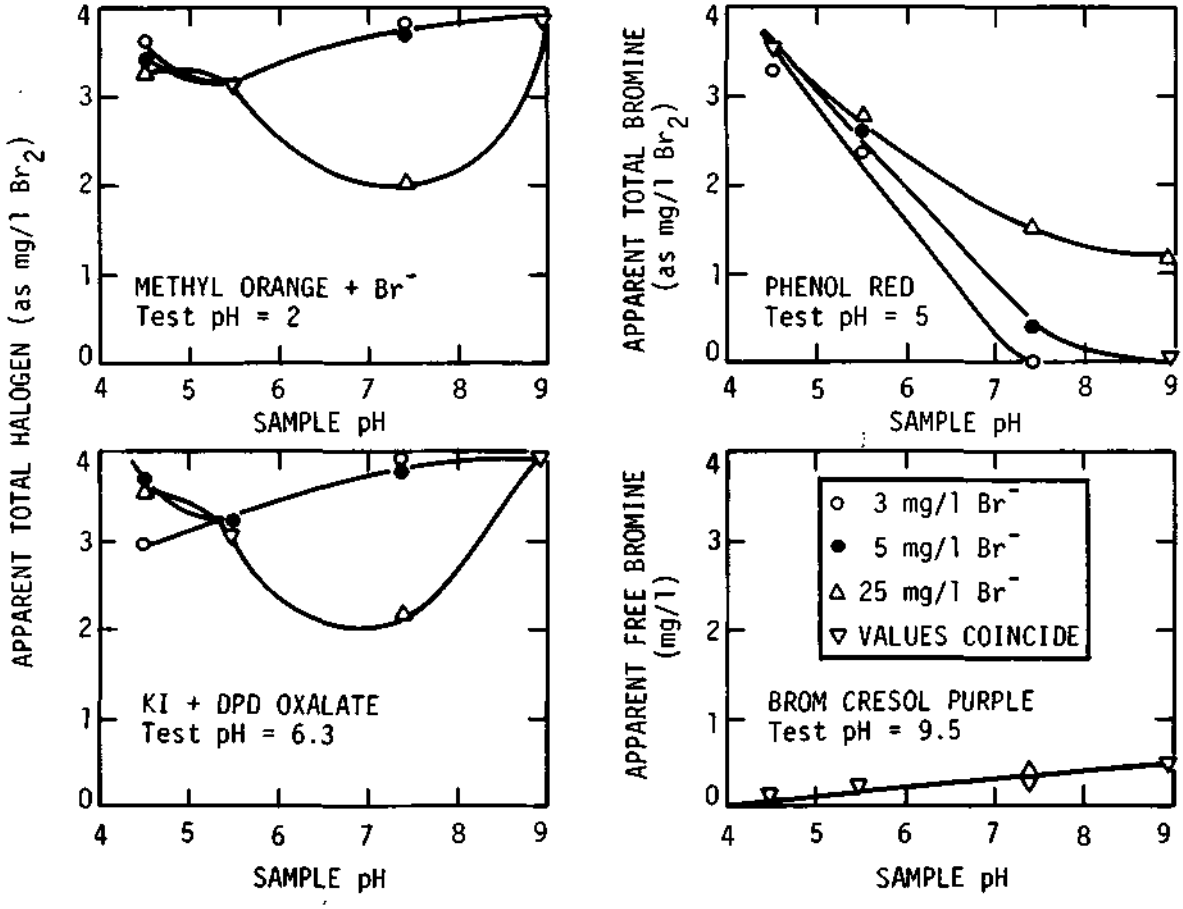


Figure 32

BROMAMINE FORMATION BY CHLORINATION OF NH_3-Br^- SOLUTIONS, 10-15°C

Initial conditions:
4 mg/l NH_3 (from NH_4Cl)
3.1 mg/l Cl_2 (=6.95 mg/l as Br_2)
Bromine residuals were determined after 5 min. contact time by the MO, DPD, PR, and BCP tests

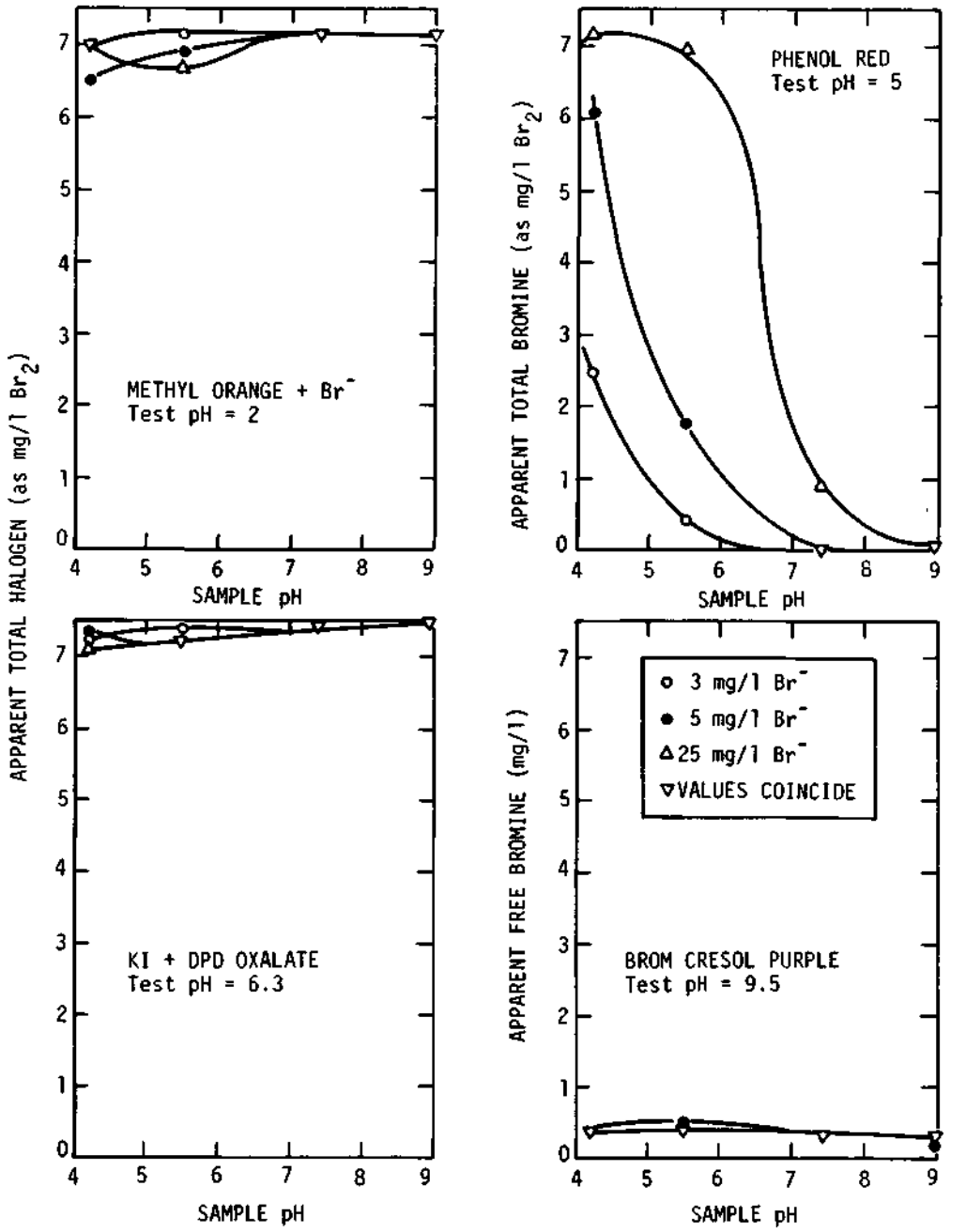
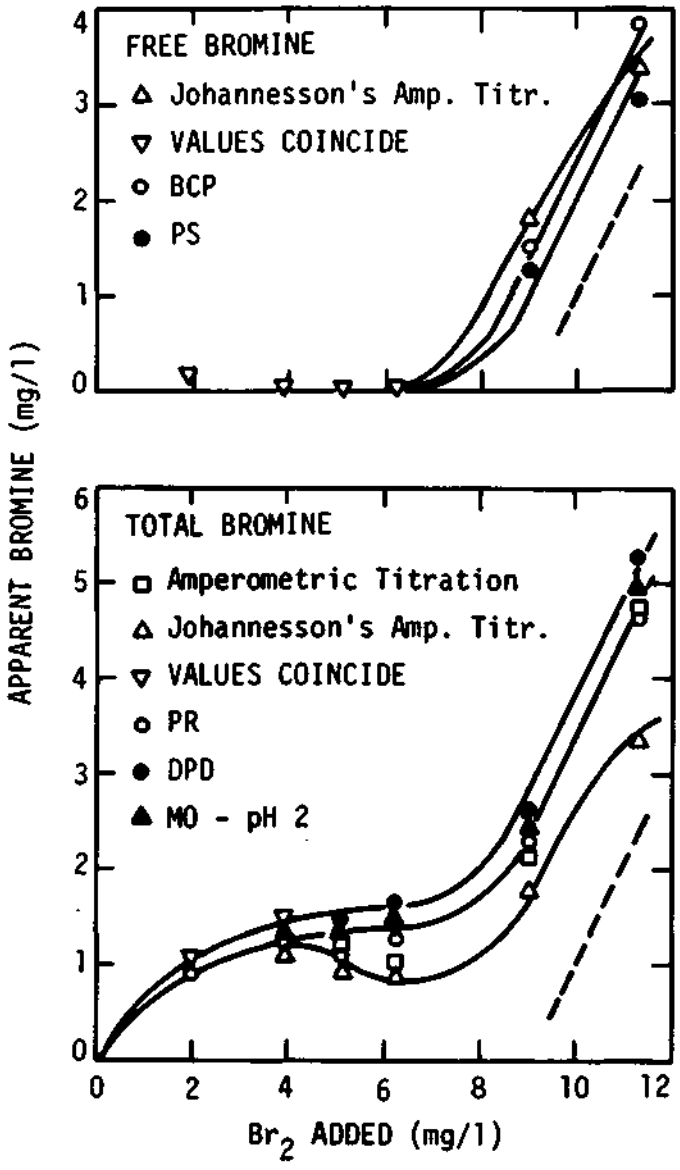


Figure 33



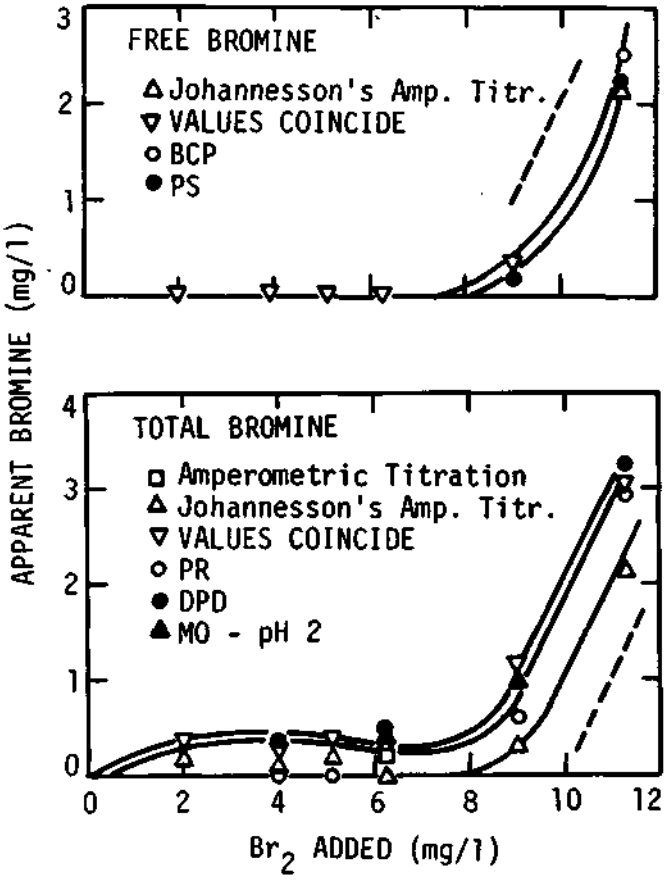
BROMINE DEMAND

1.146 mg/l Ammonium Chloride
(0.3 mg/l N)

1 HOUR REACTION TIME
pH 7.0-7.5, 26 °C

ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 34



BROMINE DEMAND

1.146 mg/l Ammonium Chloride
(0.3 mg/l N)

24 HOURS REACTION TIME
pH 7.0-7.5, 26°C

ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 35

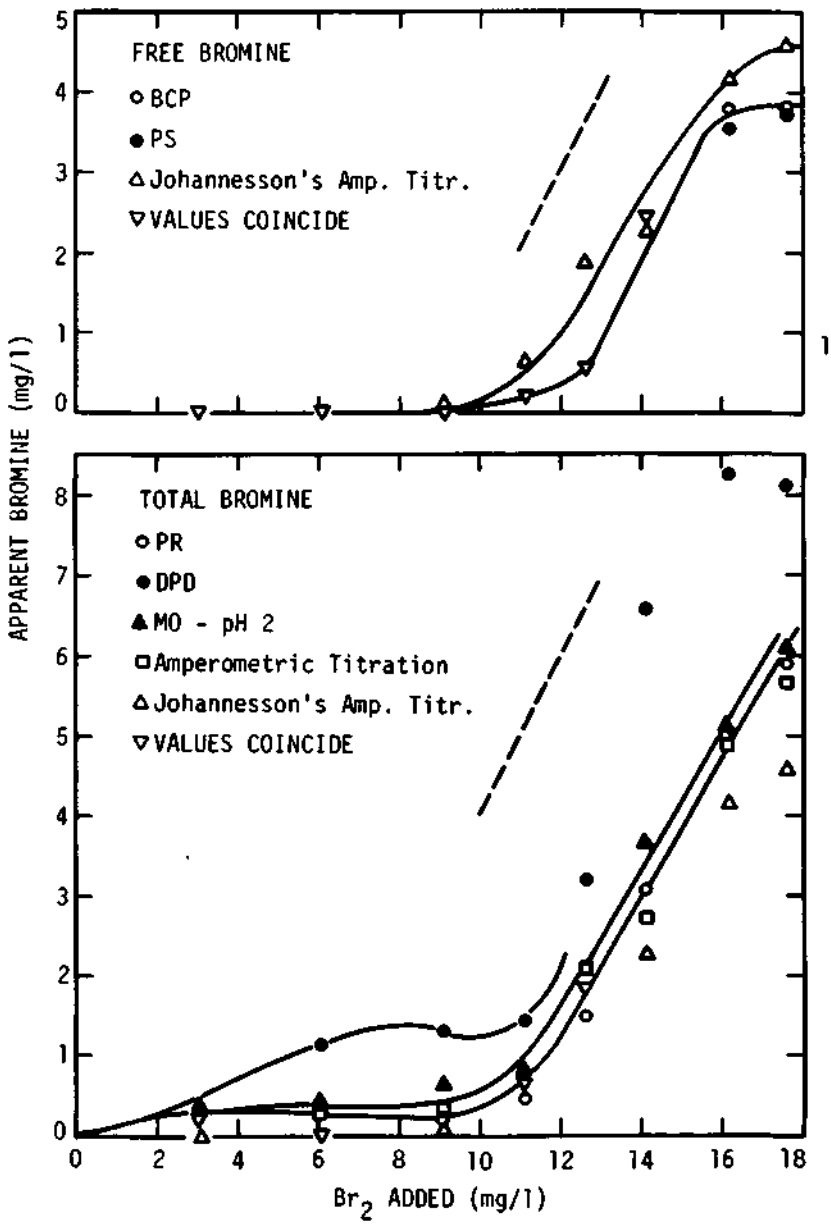

FREE BROMINE
○ BCP
● PS
△ Johannesson's Amp. Titr.
▽ VALUES COINCIDE
TOTAL BROMINE
○ PR
● DPD
▲ MO - pH 2
□ Amperometric Titration
△ Johannesson's Amp. Titr.
▽ VALUES COINCIDE
APPARENT BROMINE (mg/l)
Br_2 ADDED (mg/l)
BROMINE DEMAND
1.608 mg/l GLYCINE
(0.3 mg/l N)
1 HOUR REACTION TIME, 26°C
pH 6.5 - 6.8
ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 36

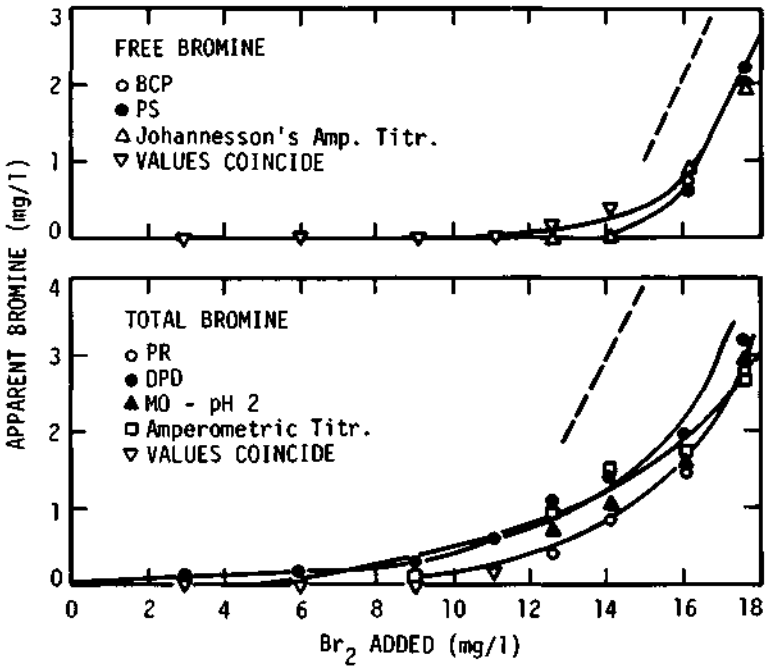
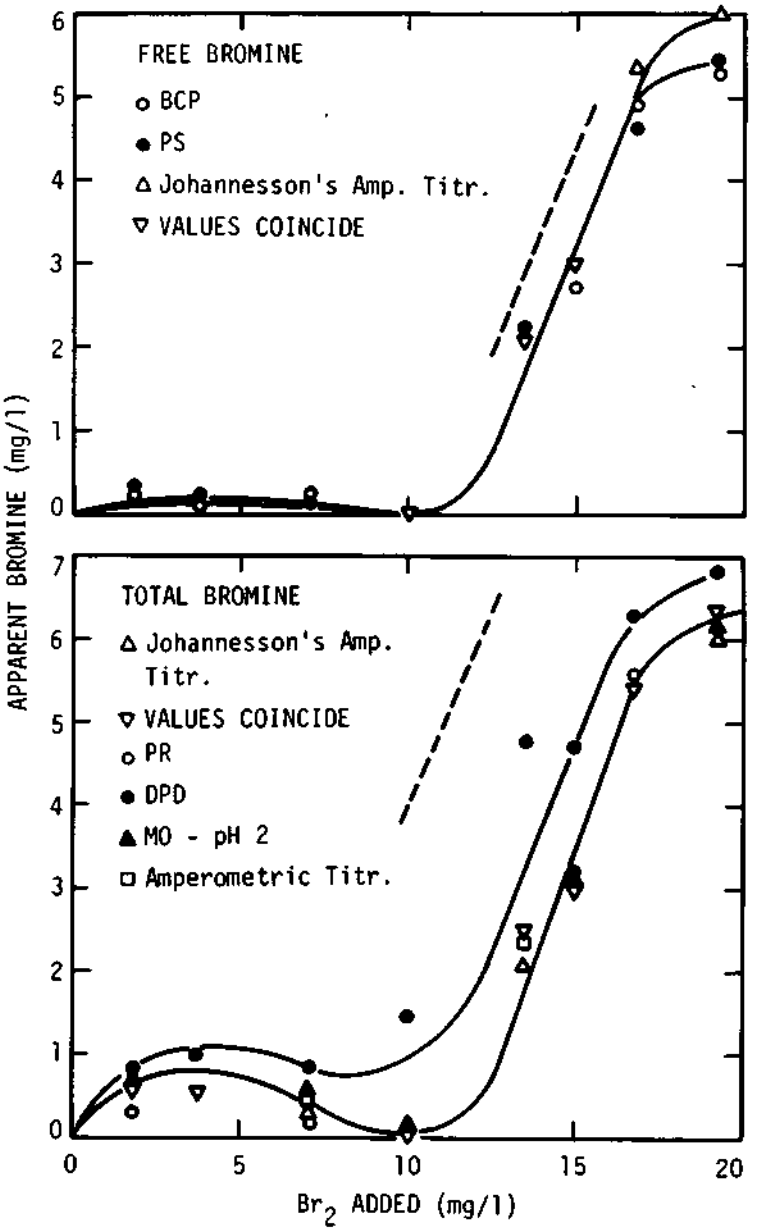

FREE BROMINE
o BCP
● PS
△ Johannesson's Amp. Titr.
▽ VALUES COINCIDE
TOTAL BROMINE
o PR
● DPD
▲ MO - pH 2
□ Amperometric Titr.
▽ VALUES COINCIDE
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)
BROMINE DEMAND
1.608 mg/l GLYCINE
(0.3 mg/l N)
24 HOURS REACTION TIME, 26°C
pH 6.5 - 6.8
ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 37



BROMINE DEMAND

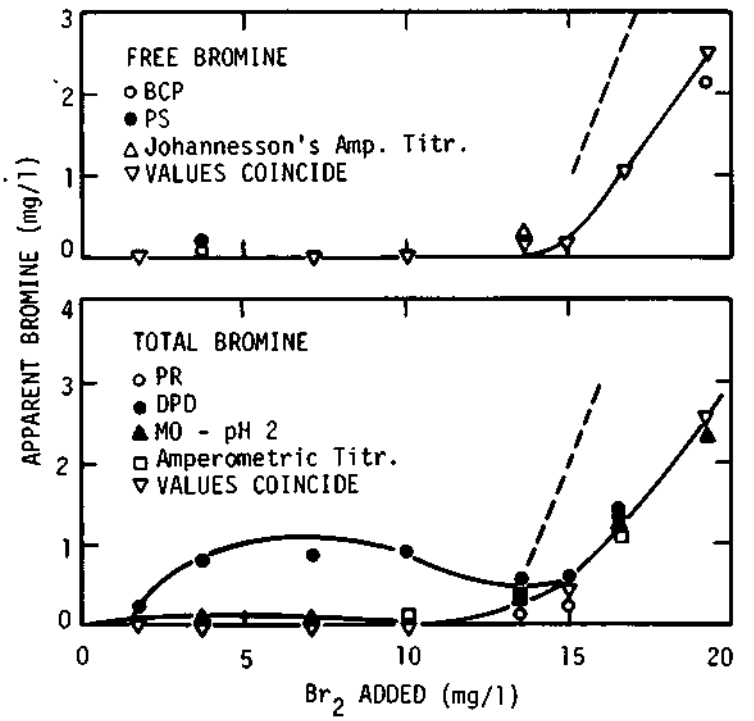
1.608 mg/l GLYCINE
(0.3 mg/l N)

1 HOUR REACTION TIME, 26°C

pH 8.0 - 8.2

ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 38



BROMINE DEMAND

1.608 mg/l GLYCINE
(0.3 mg/l N)

24 HOURS REACTION TIME, 26°C

pH 8.0 - 8.2

ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 39

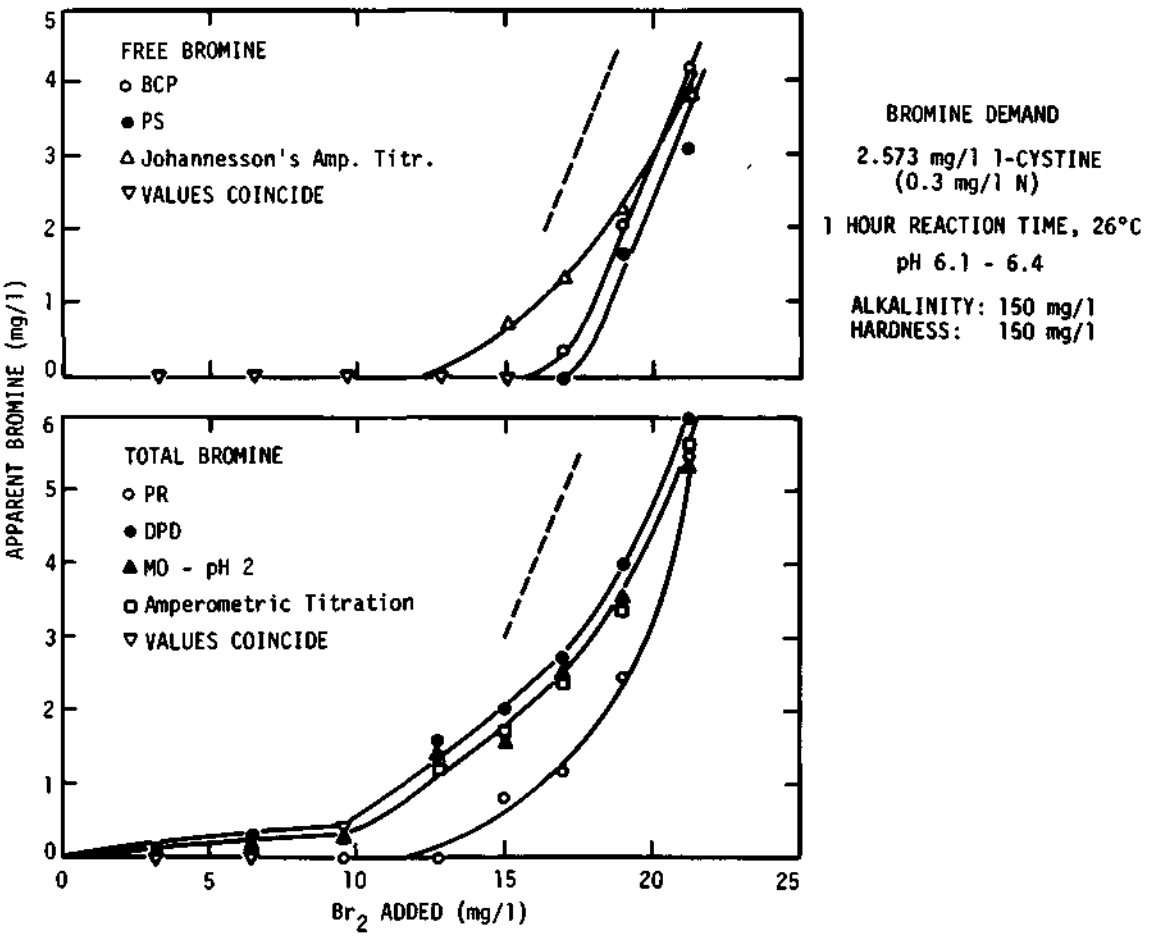

FREE BROMINE
o BCP
● PS
Δ Johannesson's Amp. Titr.
▽ VALUES COINCIDE
TOTAL BROMINE
o PR
● DPD
▲ MO - pH 2
o Amperometric Titration
▽ VALUES COINCIDE
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)
BROMINE DEMAND
2.573 mg/l l-CYSTINE
(0.3 mg/l N)
1 HOUR REACTION TIME, 26°C
pH 6.1 - 6.4
ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 40

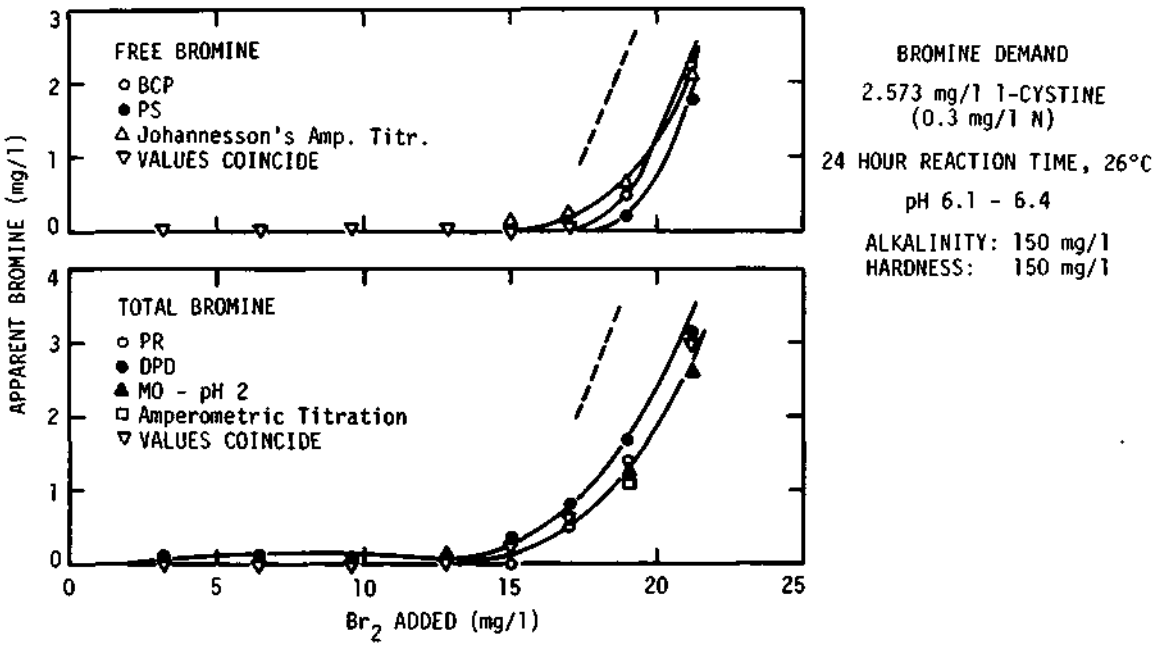

FREE BROMINE
○ BCP
● PS
△ Johannesson's Amp. Titr.
▽ VALUES COINCIDE
TOTAL BROMINE
○ PR
● DPD
▲ MO - pH 2
□ Amperometric Titration
▽ VALUES COINCIDE
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)
BROMINE DEMAND
2.573 mg/l l-CYSTINE
(0.3 mg/l N)
24 HOUR REACTION TIME, 26°C
pH 6.1 - 6.4
ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 41

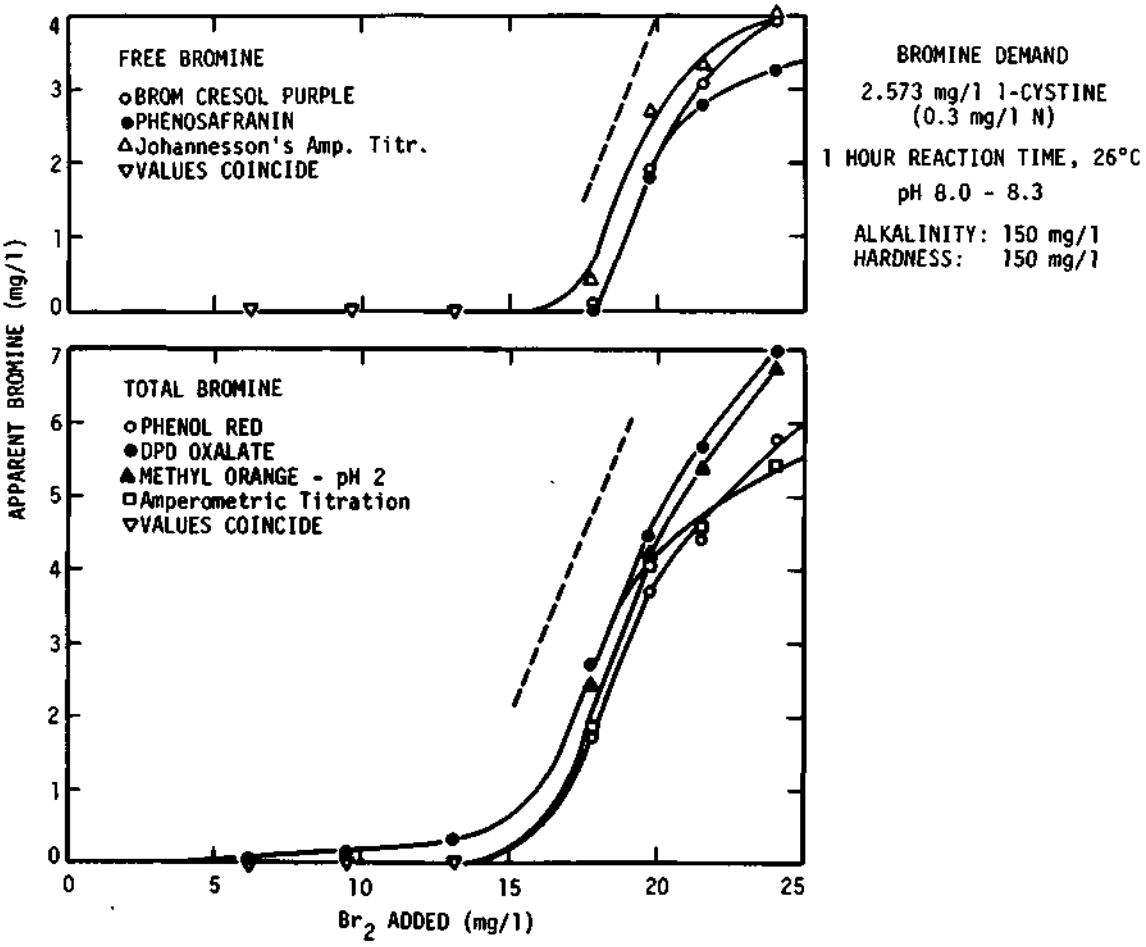

FREE BROMINE
○BROM CRESOL PURPLE
●PHENOSAFRANIN
△Johannesson's Amp. Titr.
▽VALUES COINCIDE
TOTAL BROMINE
○PHENOL RED
●DPD OXALATE
▲METHYL ORANGE - pH 2
□Amperometric Titration
▽VALUES COINCIDE
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)
BROMINE DEMAND
2.573 mg/l l-CYSTINE
(0.3 mg/l N)
1 HOUR REACTION TIME, 26°C
pH 8.0 - 8.3
ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 42

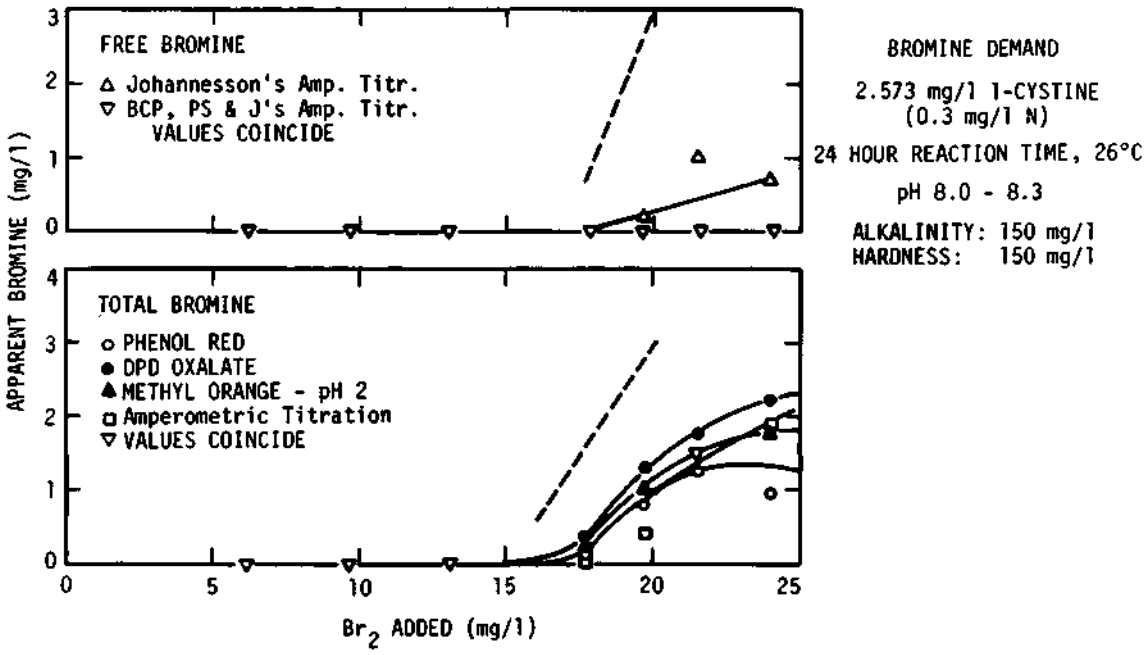

FREE BROMINE
△ Johannesson's Amp. Titr.
▽ BCP, PS & J's Amp. Titr.
VALUES COINCIDE
TOTAL BROMINE
○ PHENOL RED
● DPD OXALATE
▲ METHYL ORANGE - pH 2
□ Amperometric Titration
▽ VALUES COINCIDE
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)
BROMINE DEMAND
2.573 mg/l l-CYSTINE
(0.3 mg/l N)
24 HOUR REACTION TIME, 26°C
pH 8.0 - 8.3
ALKALINITY: 150 mg/l
HARDNESS: 150 mg/l

Figure 43

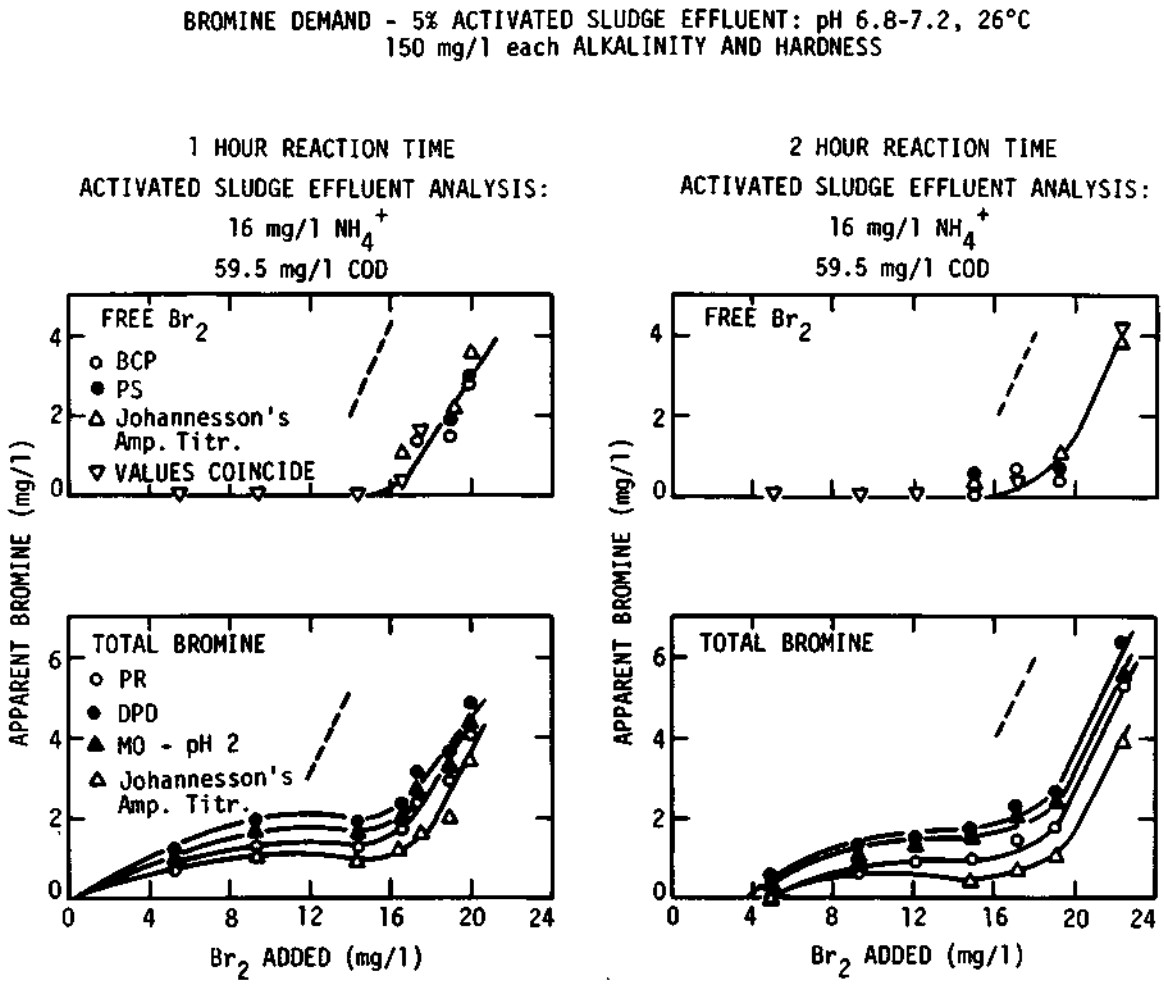

BROMINE DEMAND - 5% ACTIVATED SLUDGE EFFLUENT: pH 6.8-7.2, 26°C
150 mg/l each ALKALINITY AND HARDNESS
1 HOUR REACTION TIME
ACTIVATED SLUDGE EFFLUENT ANALYSIS:
16 mg/l NH4+
59.5 mg/l COD
2 HOUR REACTION TIME
ACTIVATED SLUDGE EFFLUENT ANALYSIS:
16 mg/l NH4+
59.5 mg/l COD
FREE Br2
BCP
PS
Johannesson's Amp. Titr.
VALUES COINCIDE
TOTAL BROMINE
PR
DPD
MO - pH 2
Johannesson's Amp. Titr.
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)

Figure 44

BROMINE DEMAND - 10% ACTIVATED SLUDGE EFFLUENT: pH 6.7-7.2, 26°C
150 mg/l each ALKALINITY AND HARDNESS

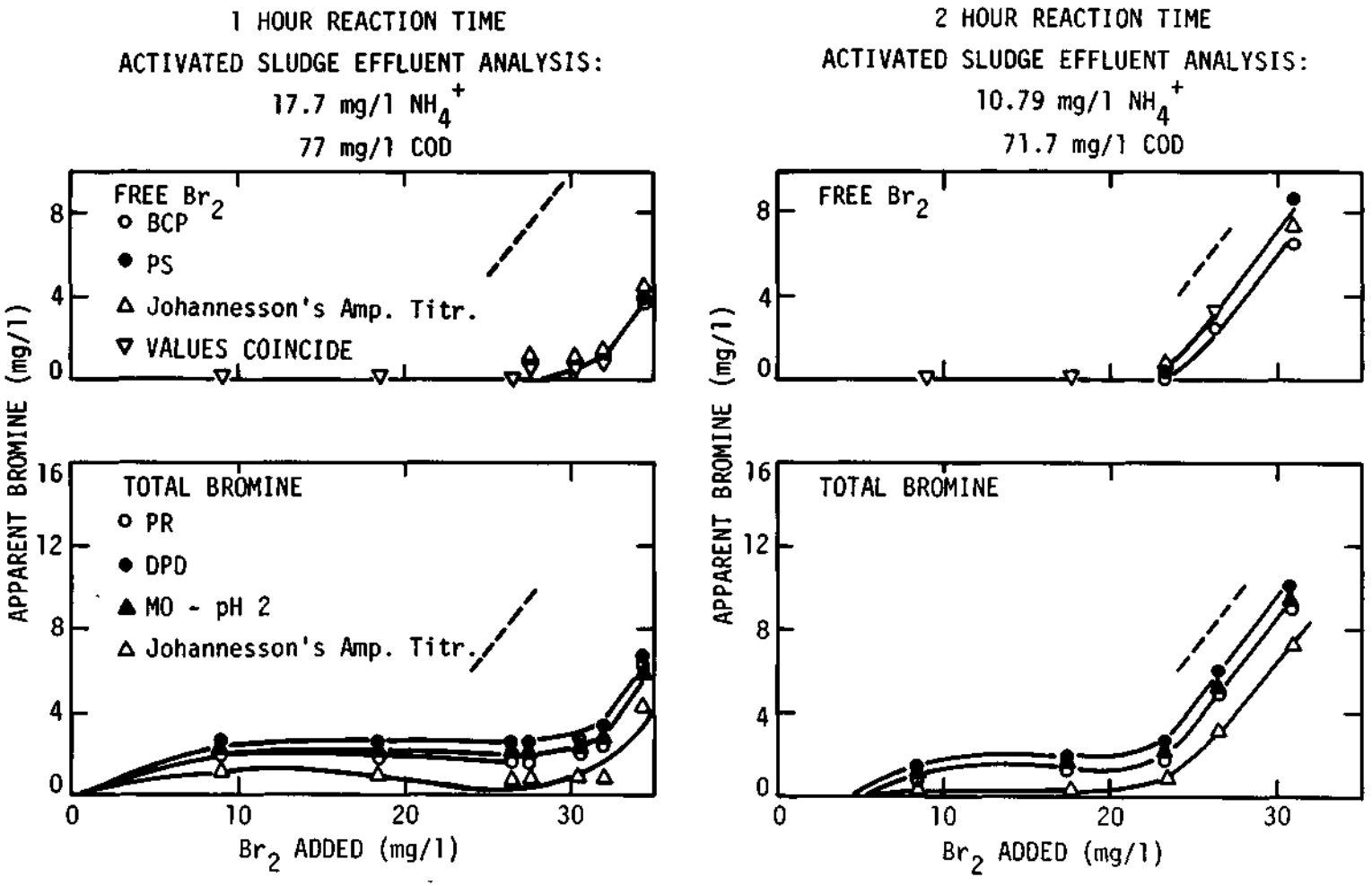
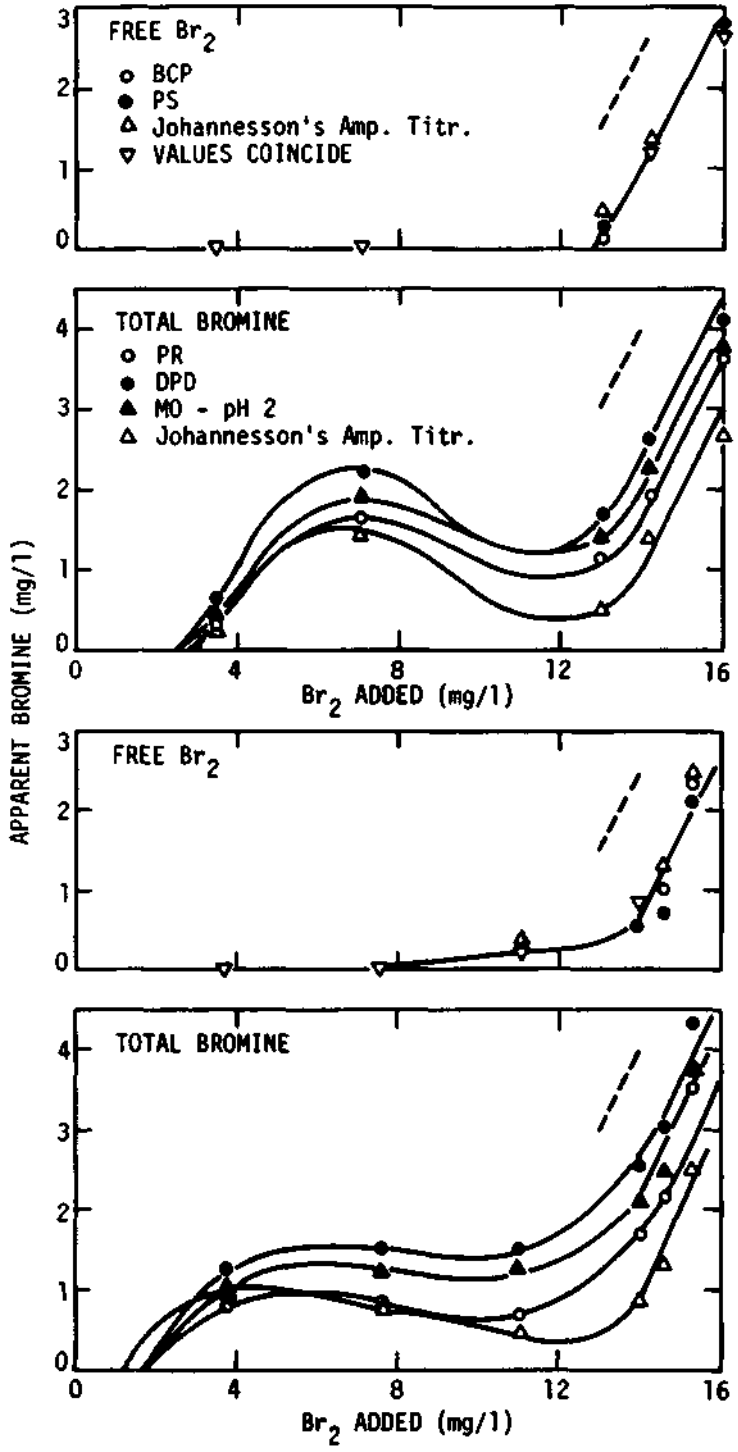


Figure 45

BROMINE DEMAND - 2% PRIMARY EFFLUENT: pH 7-7.2, 26°C
150 mg/l each ALKALINITY AND HARDNESS



1 HOUR REACTION TIME
PRIMARY EFFLUENT ANALYSIS
39 mg/l NH_4^+
272.5 mg/l COD

2 HOUR REACTION TIME
PRIMARY EFFLUENT ANALYSIS
23.65 mg/l NH_4^+
226 mg/l COD

Figure 46

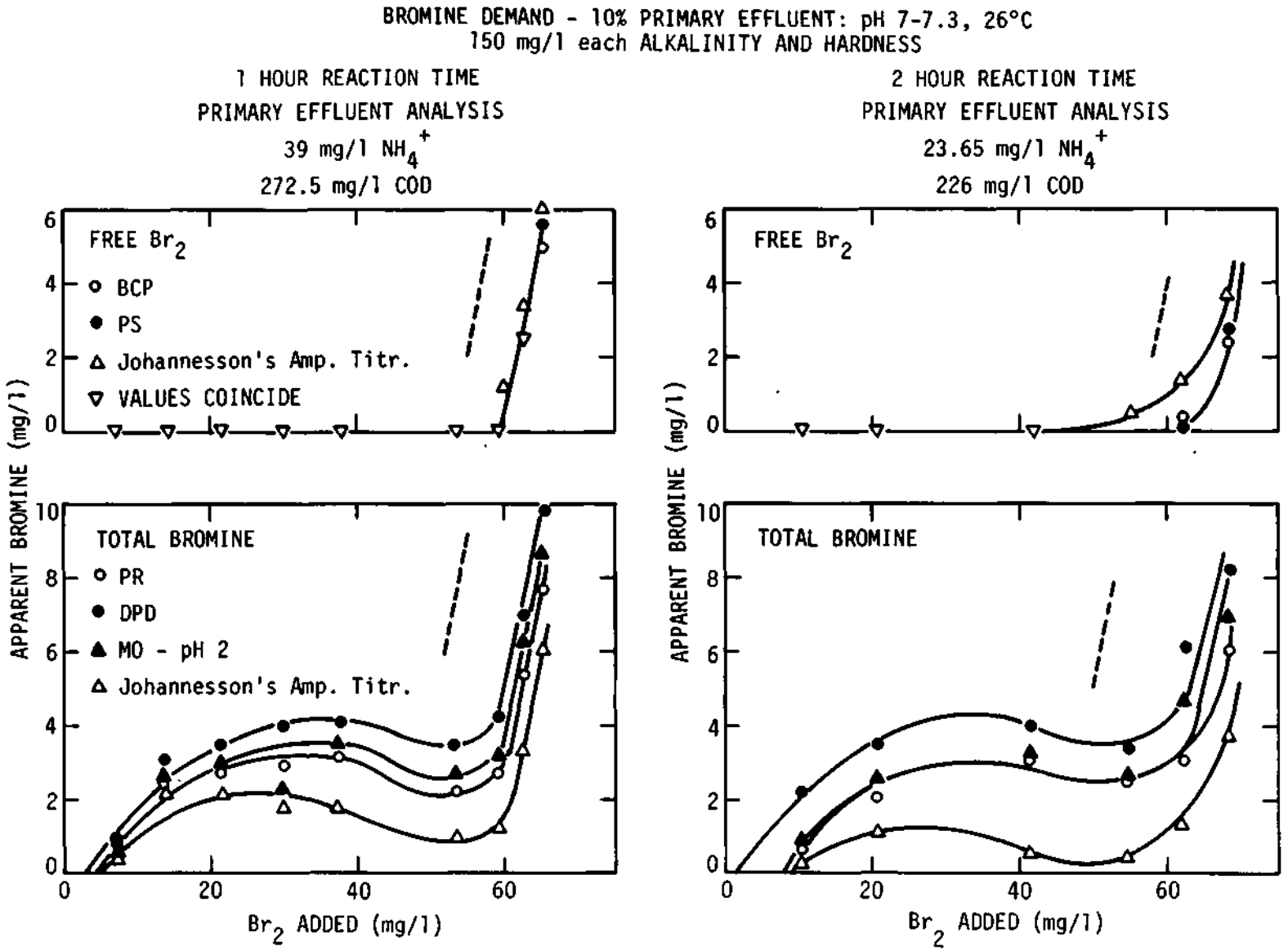

BROMINE DEMAND - 10% PRIMARY EFFLUENT: pH 7-7.3, 26°C
150 mg/l each ALKALINITY AND HARDNESS
1 HOUR REACTION TIME
PRIMARY EFFLUENT ANALYSIS
39 mg/l NH4+
272.5 mg/l COD
2 HOUR REACTION TIME
PRIMARY EFFLUENT ANALYSIS
23.65 mg/l NH4+
226 mg/l COD
FREE Br2
BCP
PS
Johannesson's Amp. Titr.
VALUES COINCIDE
TOTAL BROMINE
PR
DPD
MO - pH 2
Johannesson's Amp. Titr.
APPARENT BROMINE (mg/l)
Br2 ADDED (mg/l)

Figure 47

BROMINE DEMAND - 5% & 10% ACTIVATED SLUDGE EFFLUENT: pH 7.0-7.2, 26°C
150 mg/l each ALKALINITY AND HARDNESS

ACTIVATED SLUDGE EFFLUENT ANALYSIS: 10.4 mg/l NH_4^+, 46.5 mg/l COD

KEY: ●DPD, □Std. Amp. Titr., ▲MO, △J's Amp. Titr., ○BCP, ▽VALUES COINCIDE

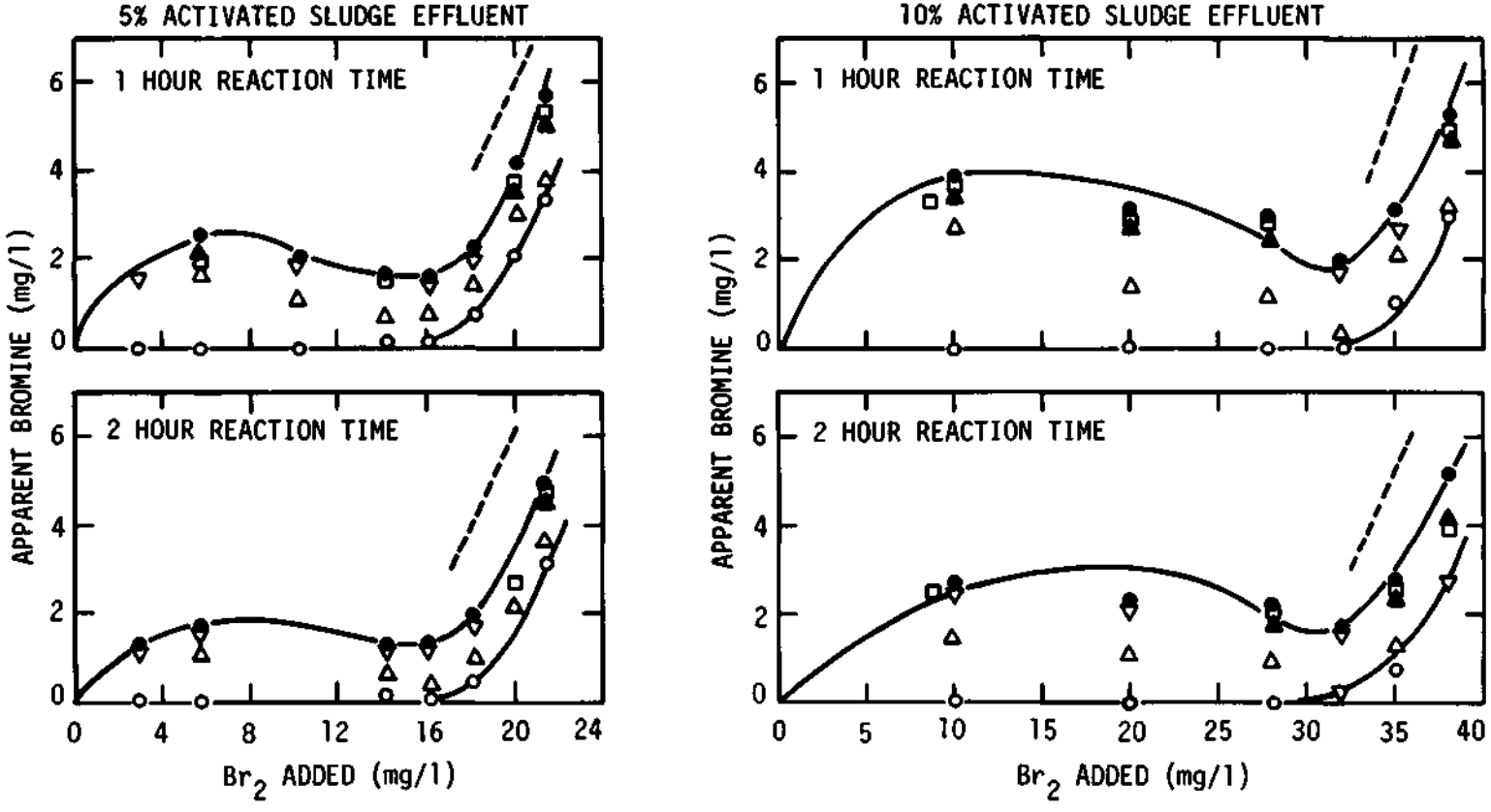


Figure 48

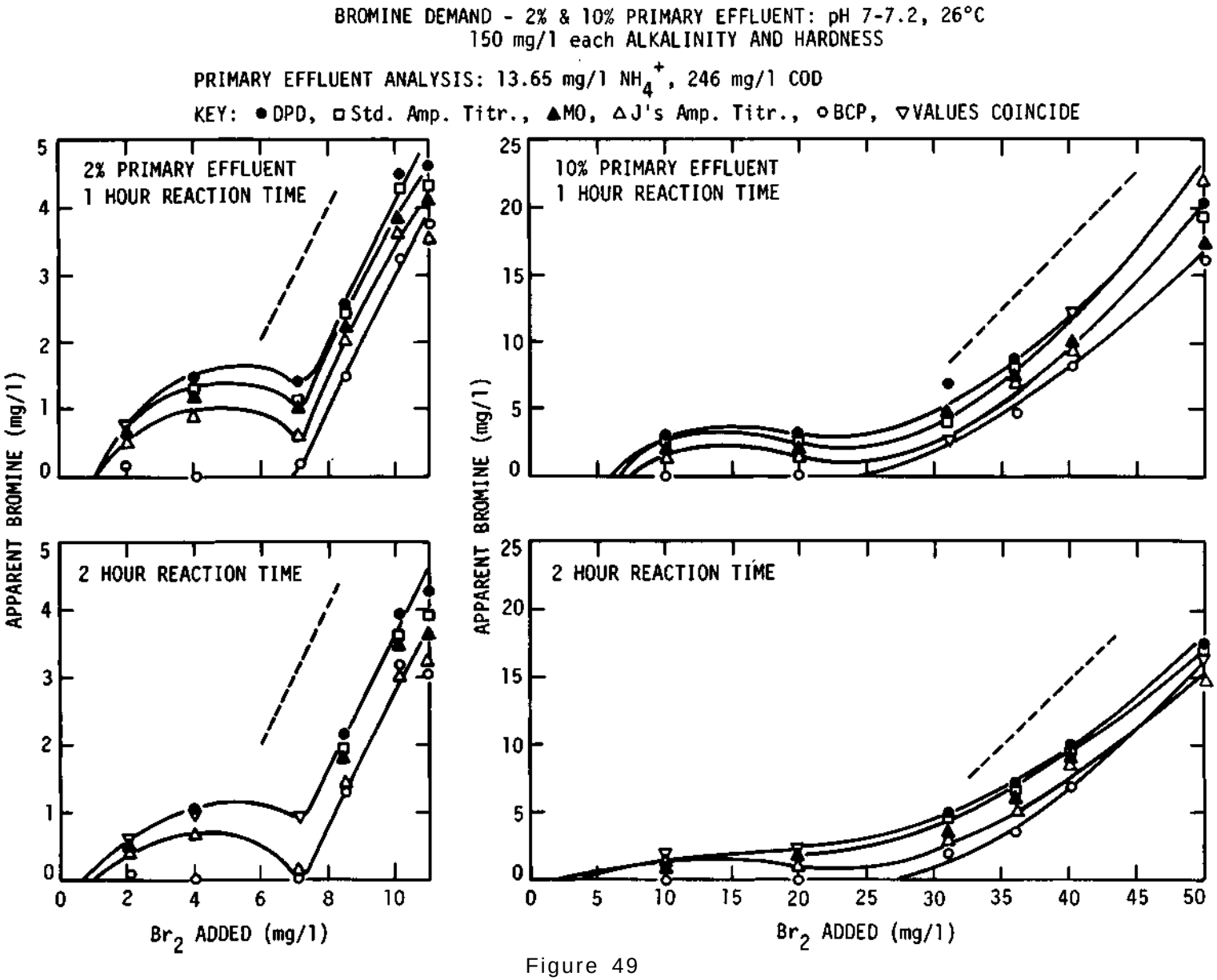

BROMINE DEMAND - 2% & 10% PRIMARY EFFLUENT: pH 7-7.2, 26°C
150 mg/l each ALKALINITY AND HARDNESS
PRIMARY EFFLUENT ANALYSIS: 13.65 mg/l NH_4^+, 246 mg/l COD
KEY: ● DPD, □ Std. Amp. Titr., ▲ MO, △ J's Amp. Titr., ○ BCP, ▽ VALUES COINCIDE
2% PRIMARY EFFLUENT
1 HOUR REACTION TIME
10% PRIMARY EFFLUENT
1 HOUR REACTION TIME
2 HOUR REACTION TIME
2 HOUR REACTION TIME
APPARENT BROMINE (mg/l)
APPARENT BROMINE (mg/l)
Br_2 ADDED (mg/l)
Br_2 ADDED (mg/l)

Figure 49

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
UNIVERSITY OF ILLINOIS
Urbana, Illinois

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DETERMINATION OF FREE BROMINE IN WATER

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13. ABSTRACT

The major objective of this work has been the development of suitable analytical 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, chloramines, and bromamines. 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.

Bromine-ammonia and chlorine-ammonia breakpoint curves have been determined for varied contact times and at different pH values. The reaction of bromine appears to be more rapid than that of chlorine, especially at high pH.

Studies of the stability under varying ammonia-to-br'omine ratios and varying pH values indicate that the bromamines are far less stable than the chloramines.

The six colorimetric reagents listed above have been examined for response to mono-, di-, and tribromamine. To insure a minimum amount of reaction of the bromamines with the BCP, PS, and MO (pH 9.5)

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reagents, the premixed buffer and sample must be added to these reagents. To obtain a maximum response to the bromamines, specifically NBr_3, potassium iodide must be added to the sample prior to testing with DPD. The response of the MO and PR tests to the bromamines is complete.

Studies made of the reactions of chlorine in buffered solutions containing varying concentrations of ammonia and bromide ion indicate that the reaction to form bromamines depends primarily upon pH.

A number of vthe selected methods have been evaluated for their performance in water containing ammonia and amino acids. This was a preliminary to a study of their performance in polluted water. In both studies, brom cresol purple and phenosafranin were in reasonably good agreement for the free bromine determinations. In the determination of total available bromine, DPD gave the highest values followed by methyl orange (pH 2) and phenol red. In both studies the breakpoint curves determined by these methods were also compared with similar curves determined by two different amperometric titration procedures.

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Analysis						
Water						
Disinfection						
Bromine						
Methyl Orange						
N,N-diethyl-p-phenylene diamine oxalate						
Phenol Red						
Brom Cresol Purple						
Phenosafranin						

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