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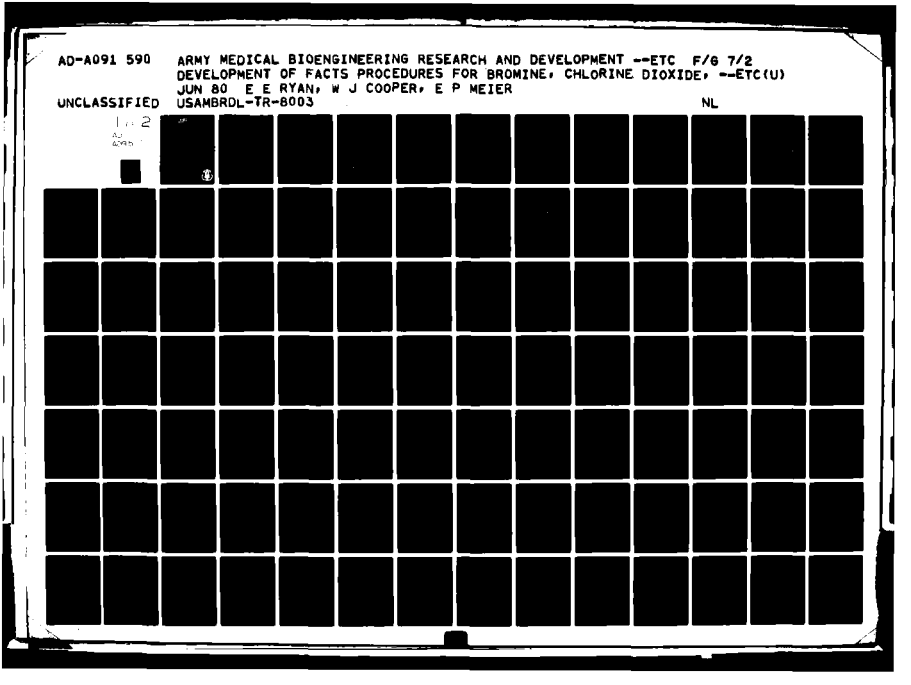

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(6) DEVELOPMENT OF FACTS PROCEDURES FOR BROMINE, CHLORINE DIOXIDE, AND IODINE IN AQUEOUS SOLUTIONS

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Chlorine has been shown to produce toxic and potentially carcinogenic compounds when used for water and wastewater disinfection. Alternative disinfectants are being investigated for use in water and wastewater. This study describes the research leading to the modification of the FACTS II procedure to give a procedure for determining several alternative disinfectants -- bromine, chlorine dioxide, and iodine -- in aqueous solution.

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The modified FACTS II procedure obeys Beer's Law through a range of 0 to 26 mg/L bromine (as Br_2) and 0 to 18.2 mg/L chlorine dioxide (as ClO_2), and the FACTS II procedure with dilution obeys Beer's Law through the range of 0 to 31 mg/L iodine (as I_2).

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INTRODUCTION

Disinfection is necessary to control the transmission of waterborne pathogenic organisms in drinking water and wastewater. Rapid, accurate, and precise determination of the concentration of disinfectant in the treated water is important for adequate control. Low disinfectant concentrations in a water distribution system or a wastewater treatment effluent may increase the risk to human health because of the presence of pathogenic organisms. Excess disinfectant concentration is an unnecessary economic burden on the treatment operation and can in itself be a health hazard.

Chlorination as a process of disinfection has been practiced in the United States since the early 1900's. Today, chlorination accounts for approximately 95% of all the disinfection processes used in the United States.

Recently, it has been demonstrated that chlorine reacts with naturally occurring organics during the water treatment process to produce chlorinated hydrocarbons, which are suspected to be carcinogens in human beings. In wastewater treatment, the addition of chlorine results in combined or free residuals, which may adversely affect the aquatic organisms in the receiving water.

Because of the above concerns, there are widespread efforts to evaluate alternative disinfectants for both water and wastewater treatment. The alternative disinfectants being investigated include bromine, bromamines, iodine, ozone, and chlorine dioxide. Means of determining the concentrations of these alternative disinfectants are needed; the present study satisfies this need.

LITERATURE REVIEW

Chlorine

Chlorine was utilized in water treatment as early as 1908.[1] At first, sodium or calcium hypochlorite was employed; however, as technology improved, chlorine in the gaseous form became generally accepted. In addition to its application as a disinfectant, chlorine has been used to control taste and odor, prevent algal growth, oxidize inorganic compounds, and reduce color in waters.

Chlorine gas reacts with water in a mobile equilibrium according to Equation 1:

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl \qquad (1)$$

Free available chlorine (FAC) is defined as the sum of the Cl_2, HOCl, and OCl^- in water, but significant concentrations of elemental Cl_2 are present only at very low pH.[2] The distribution of HOCl and OCl^- is also pH dependent, according to Equation 2:

$$HOCl \rightleftarrows H^+ + OCl^-, \quad K_a = 2.6 \times 10^{-8} \text{ at } 20°C \qquad (2)$$

HOCl is a better disinfectant than OCl^-.[2] Because of this, the disinfection process requires pH control. In addition to the reaction in water in Equation 1, chlorine can react with ammonia to form monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). These compounds are collectively referred to as combined available chlorine (CAC) and will be discussed in greater detail in connection with the breakpoint phenomenon.

The reaction of chlorine with ammonia under water treatment conditions involves a complex behavior known as the breakpoint phenomenon.[3,4] A breakpoint experiment consists of the addition of various doses of chlorine to identical samples of water containing ammonia or amines; after a specified period of time (2 hours), the total available chlorine in each reaction mixture is measured. (Total available chlorine is defined as the sum of the FAC and CAC, and is determined by titration with a reducing agent after addition of iodide.)

During the 2-hour incubation, a number of reactions occur (Equations 3-10). As shown by Figure 1, some of the chlorine initially added is lost at all points along the curve. This loss is attributable to reactions such as those shown in Equations 7-10. However, these loss reactions occur much more rapidly in the vicinity of point C, the breakpoint, than at point A, where monochloramine predominates (at the end of 2 hours), or at point B, where a significant proportion of dichloramine can be observed after the 2-hour incubation.

Beyond breakpoint, the ammonia and organic amines are almost completely destroyed, although part of the chlorine and ammonia may remain in the form of trichloramine.

At all points along the curve until the breakpoint has been exceeded, the disinfection capability of the combined chlorine species that comprise the major part of the total available chlorine is considerably less than that of FAC. The inefficiency of CAC varies from organism to organism.

$$HOCl + NH_3 \rightarrow H_2O + NH_2Cl \qquad \text{Monochloramine} \qquad (3)$$

$$HOCl + NH_2Cl \rightarrow H_2O + NHCl_2 \qquad \text{Dichloramine} \qquad (4)$$

$$HOCl + NHCl_2 \rightarrow H_2O + NCl_3 \qquad \text{Trichloramine} \qquad (5)$$

$$NCl_3 + H_2O \rightarrow NHCl_2 + HOCl \qquad (6)$$

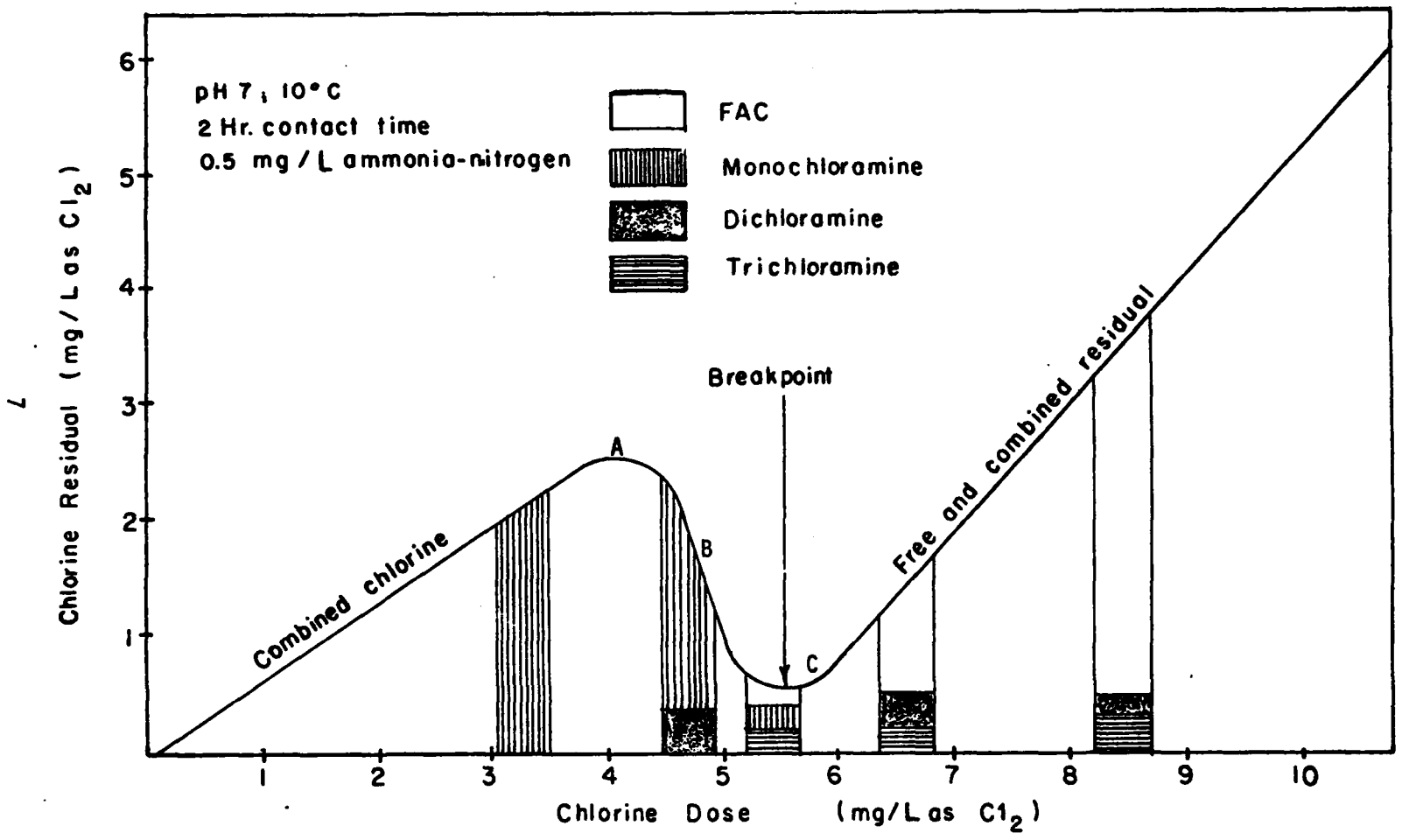


Figure 1. Breakpoint Diagram after White.[2]

$$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^- \quad \text{(postulated)} \quad (7)$$

$$NOH + NH_2Cl \rightarrow N_2\uparrow + H_2O + H^+ + Cl^- \quad \text{Denitrification} \quad (8)$$

$$NOH + NHCl_2 \rightarrow N_2\uparrow + HOCl + H^+ + Cl^- \quad \text{Denitrification} \quad (9)$$

$$NOH + 2HOCl \rightarrow NO_3^- + 3H^+ + 2Cl^- \quad (10)$$

The combined chlorines are the predominant disinfectants before the breakpoint and occur when insufficient chlorine is added. Since combined chlorine is not as effective as FAC in disinfection,[2,5-8] the breakpoint must be exceeded to disinfect the treated water properly.

Although chlorine is an excellent disinfectant, there are two serious problems with its use in water (or wastewater) treatment.

(1) Chlorine reacts with certain naturally occurring organic contaminants of water supplies, certain industrial pollutants, and domestic waste components to form organochlorine compounds that are suspected of being carcinogenic to humans. One class of such carcinogens is the trihalomethanes.[9-11]

Rook has extensively studied the products of chlorination of natural waters.[9,12,13] Humic acids are a major portion of the soluble organics and appear to react with chlorine to produce trihalomethanes. The reaction proceeds to a measurable extent even at low doses of chlorine. Bellar and co-workers[14] have shown that the concentration of trihalomethanes increases with chlorine contact time and that chloroform levels increase further with each chlorine addition.

Long-term health effects from the ingestion of organochlorine compounds are being studied. The trihalomethanes may indicate a larger potential problem[11] with other chlorinated compounds of higher molecular weight. Chlorinated hydrocarbons resist degradation in water and could accumulate in fatty tissue.[15]

(2) In wastewater treatment, residual chlorine can also be toxic to fish and other aquatic organisms.[16-22] Toxicity to fish depends on the amount of residual chlorine and the receiving water conditions. The suggested water quality criterion for protection of continuously exposed freshwater life,[16] 0.003 mg/L, is widely accepted.[17] Toxicity to fish may result in a shift in the proportion of different fish species and can upset the ecological balance of the receiving water.[22,23] Because of these disadvantages, chlorine's use as a disinfectant is being questioned and studied.[10,16,19,24]

Bromine

Problems with hypochlorinators have led the US Navy to search for alternate methods of shipboard disinfection. Calcium hypochlorite, $Ca(OCl)_2$, gives off dangerous chlorine gas; moreover, the chlorinators are unreliable.

For these reasons, the Navy has introduced bromine adsorbed on a resin as a disinfectant for potable water on surface ships. Bromine was tested on ships from March 1969 to May 1971 and the results were acceptable.[25] From these tests and the literature,[26-31] the Navy concluded that there was no danger to humans, and began using bromine on all surface ships.

Bromine reacts with ammonia to form bromamines in a phenomenon similar to breakpoint chlorination. However, unlike the chloramines, bromamines have been shown to be good disinfectants.[32-34] In addition, bromamines degrade much faster than chloramines, thus reducing residual toxicity in effluent waters. Bromine is also more effective than chlorine at the higher pH values of some natural waters. Bromine is competitive with chlorine in disinfection capability,[35-37] and is a better viral disinfectant than chlorine.[32,38] The bromamines are also equivalent to free bromine in disinfectant ability for several forms of bacteria and viruses.[33,37,38] The major disadvantage of bromine is that it is more expensive to use than chlorine.

Bromine chloride is less expensive than pure bromine, although equivalent to bromine in its activity as a water disinfectant, and can partially overcome bromine's economic disadvantage.[32,35,38] Bromine chloride reacts with water in a mobile equilibrium in essentially the same way as chlorine, shown in Equation 1. Most of the bromine from dissociation of this compound forms the highly effective disinfectant hypobromous acid, HOBr, and most of the chlorine forms hydrochloric acid, HCl. There is little or no formation of hydrobromic acid, HBr, or hypochlorous acid, HOCl.[35] In this way, the more expensive component, bromine, is the actual disinfectant; and the cheaper component, chlorine, plays no role in the disinfection process.

In 96-hour acute survival tests in diluted wastewater effluent treated with bromine chloride, all fish survived.[32,38] In wastewater, bromine chloride is a more active and faster bactericide and virucide than chlorine. In the presence of ammonia, Polio II virus was sterilized in less than 5 minutes with 4 mg/L bromine chloride. An equivalent concentration of chlorine failed to kill all the virus in more than 60 minutes.[35,38]

Chlorine Dioxide

The major use of chlorine dioxide is as a bleach in the paper and the flour industries[39,40] because it produces a better product than other bleaches. It is also used in the treatment of potable water for taste and odor control.[41] A 1958 survey of drinking water treatment plants that used chlorine dioxide revealed that the plant operators felt chlorine dioxide was a good disinfectant.[42] It is the best disinfectant choice where tastes are a problem.[42,43] Chlorine dioxide has been reported to be a considerably better disinfectant for Escherichia coli and spores than chlorine.[44] It is reportedly better than chlorine for total coliforms and fecal streptococcus, and for ϕX174 and f_2 viruses.[45-49] Unlike chlorine or bromine, chlorine dioxide does not react with ammonia, thus reducing the amount of chlorine dioxide needed for wastewater treatment.[45,50,51]

Studies have shown that a two-stage disinfection process, using chlorine as the first stage and chlorine dioxide as the second stage, is superior to either stage alone.[44,46] Lower doses of both disinfectants may be used to obtain equivalent disinfection. The bactericidal and virucidal efficiencies of 12 mg/L chlorine dioxide or of 25 mg/L chlorine were equivalent to the efficiency of 8 mg/L chlorine followed by 2 mg/L chlorine dioxide.[46]

Chlorine dioxide does not form chloroform or other trihalomethanes, nor does it produce the characteristic taste and odor of chlorinated phenol with water containing traces of phenolic compounds.[17,45,46,51] Chlorine dioxide forms fewer chlorinated products than chlorine does. Although reactive with organic amines, it does not react with ammonia.[51-56] Therefore, breakpoint chlorination is not needed with chlorine dioxide in order to have sufficient disinfection.

A disadvantage of chlorine dioxide is that it has to be generated on site. The chemicals needed for this process are readily available, but existing delivery systems are not always acceptable.

Iodine

Iodine has been used by the military to disinfect individual water supplies in emergency situations.[57,58] A rapidly soluble tablet form consistently provides 5 to 10 mg/L of elemental iodine. Iodine has been used to disinfect swimming pools,[59] and has been studied for its effectiveness in public water supplies.[57,58,60] As iodine does not react with ammonia in water,[58,59] its disinfectant qualities are not affected by the presence of ammonia.

The effect of iodine on bacteria, viruses, and amebic cysts has been studied.[58,60,61] At a pH of less than 6, the titratable iodine exists as I_2 and has been shown to be a better cysticide than virucide. Above a pH of 6, where HOI (hypoiodous acid) predominates, I_2 appears to be a more effective virucide than cysticide.

Iodine, although used for disinfection of individual water supplies, will probably not be accepted as a general disinfectant until additional testing showing its disinfection ability is completed.

Test Procedures

Quick, accurate, and precise determination of the disinfectant concentration in treated drinking water and wastewater is important. Low concentrations may not produce the required degree of disinfection. High concentrations may adversely affect the environment and economically burden the treatment operation. Thus, a specific, accurate, and precise test for monitoring disinfection of water is desirable.[62-64]

Federal law mandates 0.2 mg/L free chlorine throughout the distribution system for drinking water.[65] This is based on the EPA selection of a chlorine level that is safe for public health and also environmentally acceptable.

There is no federal standard for wastewater. Each state sets its own standard on a case-by-case basis dependent upon the subsequent use of the receiving waters.[11]

Chlorine was introduced as a disinfectant in the early 1900's. The orthotolidine test was used only as a qualitative indicator of residual chlorine until 1913, when it began to be used as a quantitative test for chlorine.[2] This test measures total chlorine residuals, but its accuracy decreases as pollutants increase.

The addition of arsenite after the orthotolidine converted the original version to the orthotolidine-arsenite (OTA) test. This was more specific for FAC than the simpler orthotolidine test, but was also dependent on the temperature and the time of the observation.[2]

Another modification was made to overcome the temperature and time dependence. This modified orthotolidine arsenite (MOTA) procedure was an improvement, but still had serious difficulties. Interfering chemicals and combined chlorine still caused erroneous results.[61,62]

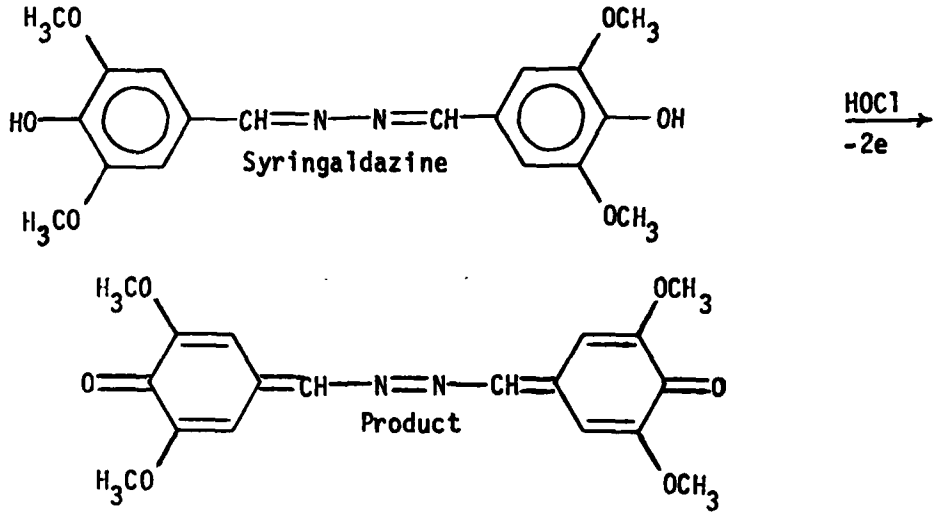
Palin first reported the N,N-diethyl-*p*-phenylenediamine (DPD) test in 1957,[2] which is reportedly capable of differentiating between FAC and CACs.[1,2,66,67] It has been modified for use with bromine, chlorine dioxide, and iodine,[67] and can be adapted to differentiate between FAC and chlorine dioxide. The DPD test does not distinguish the free form from combined forms of bromine.

Other tests that have been considered are the leuco crystal violet test, which measures free available chlorine up to 1.2 mg/L,[2,62,63] and the stabilized neutral orthotolidine test (SNORT), which has been used for concentrations between 0 and 100 mg/L[2,62,63] and is subject to interference from monochloramine.[2,61,62]

Shortly after the disclosure that vanillinazine and syringaldazine gave good results when used together for swimming pool water,[68] various test procedures for colorimetrically determining FAC were evaluated for specificity, accuracy, and precision.[63,64,69] A test using syringaldazine (without vanillinazine) was more specific than the DPD, SNORT, and leuco crystal violet tests, and the DPD test was the most accurate and precise. All the tests studied, except that with syringaldazine, gave false positive results (indications of free chlorine when none was present).[62,63]

Further studies resulted in the development of the free available chlorine test with syringaldazine (FACTS). The FACTS I procedure has a range of 0 to 8 mg/L chlorine; the FACTS II procedure has a range of 0 to 10 mg/L chlorine.[62,63,70] These procedures are excellent for determining FAC in aqueous solutions.

The color-producing reaction of the FACTS test involves the oxidation of syringaldazine to a quinone-like structure as shown in Equation 11.[71,72]



(11)

Tetramethoxy-azo-bis-methylene quinone[72]

This reaction obeys Beer's Law over a concentration range of 0 to 12 mg/L of chlorine.[73] Other strong oxidants, such as iodine and bromine, also produce a color reaction.[74]

Although the FACTS procedure was designed for FAC, the potential for determining other oxidizing species, such as the chloramines, ozone, or the alternative disinfectants such as bromine, bromamines, chlorine dioxide, and iodine, was apparent. Recently, the FACTS procedure was in fact extended for determining total chlorine and ozone.[75] However, the FACTS procedure has only now been applied to the determination of bromine, bromamines, chlorine dioxide, and iodine.

OBJECTIVES

The objectives of this research were to:

1. Modify the FACTS procedure for use in analysis of bromine (bromamines), chlorine dioxide, and iodine.

2. Determine whether the color reaction of syringaldazine with alternative disinfectants obeys Beer's Law over the desired concentration range.

3. Determine the detection limit of the developed procedure for alternative disinfectants.

4. Determine the stoichiometry of the reaction between syringaldazine and alternative disinfectants.

5. Test the procedures on organically polluted waters.

MATERIALS AND METHODS

Materials

Preparation of Chlorine Demand-Free Water (CDFW). Ten-liter bottles were filled with distilled water and 2 to 5 mL Clorox® were added. The bottles were sealed and the water was dechlorinated by exposure to sunlight for 2 days. The water was tested before use to assure that no combined or free chlorine was present.

Glassware. All glassware was cleaned with potassium dichromate/sulfuric acid solution, rinsed in chlorine water (to remove any chlorine demand), and rinsed three times with CDFW.

Preparation of FACTS II Buffer.[70,73] A stock buffer solution 0.5 M in potassium phosphate, KH_2PO_4 (Analytical Reagent, Mallinckrodt), and 0.5 M in sodium dibasic phosphate monohydrate, $Na_2HPO_4 \cdot H_2O$ (Certified grade, Fisher Scientific), was prepared in CDFW. The pH of the buffer was approximately 6.6.

Preparation of FACTS II Indicator.[70,73] Syringaldazine (Aldrich Chemical Co.), 118 mg, was dissolved in reagent grade 2-propanol and diluted to 1 liter. Dissolution of syringaldazine was aided by the use of an ultrasonic bath. These solutions were tested to verify that the response obtained with chlorine was similar to that obtained in the development of the FACTS II procedure. This was done by comparing the absorbance of a known chlorine solution with the value calculated from equations reported in earlier studies.[70] An indicator was acceptable if it produced a color within 5% of the calculated value.

FACTS II Procedure

a. A 5-mL sample of a solution of disinfectant to be tested was pipetted into chlorine demand-free test tubes. The concentration of this solution had previously been determined either by amperometric titration or by starch-iodide titration.

b. Two-tenths milliliter of the FACTS buffer (pH 6.6, 0.5 M phosphate) was added; the tube was capped and inverted twice to mix.

c. Two milliliters of FACTS indicator were added; the tube was capped and inverted twice to mix.

d. A timer was started when the first drop of indicator touched the sample.

e. The sample was transferred to a cuvette that had been rinsed three times with the reaction solution.

f. One minute after addition of the indicator, the absorbance of the solution at 530 nm was read with a spectrophotometer.

Color development and fading were monitored as a function of time.

Referee Method. Amperometric titration or starch-iodide titration (with Fisher Scientific Co. Thyodene as indicator) was used to standardize the bromine and iodine solutions. A Fischer & Porter Amperometric titrator (Model 17T1010) was used throughout the study. An ultraviolet spectrophotometer (Beckman ACTA CV) was used to standardize the monobromamine and the chlorine dioxide solutions.

Preparation of Iodine Solution. Forty grams of potassium iodide (KI) were dissolved in 10 mL of CDFW. Iodine (12.7 g) was added and the solution was stirred until the I_2 completely dissolved. The solution was filtered through a sintered glass filter, diluted to 1 liter, and stored in an amber bottle. This solution contained approximately 6,450 mg/L or 0.05 M iodine.

Preparation of Bromine Solution. One-half milliliter of liquid bromine was added to approximately 1 liter of CDFW. Then 76 g of potassium bromide (KBr) were added to bring the bromine into solution as the tribromide ion. This solution was stored in an amber bottle. The solution concentration was approximately 1,400 mg/L or 0.00876 M bromine.

Preparation of pH 7.98 Buffer. Sodium bicarbonate, $NaHCO_3$ (8.4 g), was dissolved in 100 mL CDFW to yield a 1 M stock solution (pH 7.98).

Preparation of Monobromamine (NH_2Br).[76] Ten milliliters of the 1 M pH 7.98 buffer were pipetted into a 100-mL volumetric flask and approximately 1.3 g ammonium chloride (NH_4Cl) crystals were added. Five milliliters of stock bromine solution were added slowly to the buffered ammonia solution while the buffer solution was being mixed. Chlorine demand-free water was added to bring the volume to 100 mL. This procedure gave a solution of about 30 to 40 mg/L NH_2Br (monobromamine). This monobromamine solution was made just before use. The concentration of monobromamine can be determined using Beer's Law:

$A = \varepsilon bc$

A = absorbance (measured using the Beckman ACTA CV ultraviolet spectrophotometer)

ε = molar absorptivity[76] (390 cm^{-1} liter/mole) at λ_{max} = 278

b = cell path length (cm)

c = concentration (moles/liter)

Organically Polluted Water. Samples of organically polluted water were obtained from the US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, Maryland. This wastewater had undergone primary settling and secondary activated sludge treatment, but had not been chlorinated. The samples from the pilot sewage treatment facility are characterized in Table 1. The treated sewage effluent was diluted approximately 1:1 with dechlorinated tap water for breakpoint bromination studies.

TABLE 1. CHARACTERIZATION OF ORGANICALLY POLLUTED WATER

13 February 1978	
pH	6.85
Suspended solids	36 mg/L
Total organic carbon	43 mg/L
Inorganic carbon	21 mg/L
Organic carbon	22 mg/L
Ammonia nitrogen	10 mg/L
10 March 1978	
pH	6.85
Suspended solids	87 mg/L
Alkalinity	159 mg/L
Ammonia nitrogen	13.2 mg/L

The ammonia (NH_3) concentration of the organically polluted water (before dilution) was determined with an ammonia electrode. It was found that the natural water contained about 10 mg/L NH_3 (as nitrogen). This was diluted with CDFW for breakpoint bromination tests and aerated to maintain aerobic conditions.

Breakpoint with Bromine. Known quantities of the stock bromine solution were added to the diluted organically polluted water to make a total volume of 1 liter. The solution was shaken and allowed to stand for at

least 1 hour. The concentration of the residual bromine was determined either amperometrically with 5.64×10^{-3} N phenylarsine oxide or by starch-iodide titration with 1.01×10^{-2} N sodium thiosulfate.

Preparation of Chlorine Dioxide (ClO_2).[42] Potassium persulfate (6 g), $K_2S_2O_8$, and sodium chlorite (2 g), $NaClO_2$, were combined and added to 50 mL of distilled water. The resultant slurry was stirred with a magnetic stirrer for 15 to 20 seconds and then poured into the reaction flask. Nitrogen gas was bubbled through the reaction flask to carry the gaseous ClO_2 into the collection flask. The collection flask (containing 100 mL of cold CDFW) was kept cold in an ice bath. The gaseous ClO_2 was trapped in the cold water (Figure 2).

One hour of reaction gave a solution of 2,000 to 3,000 mg/L; 4 hours of reaction gave a solution of 3,000 to 4,000 mg/L. The ClO_2 solution was stored in a refrigerator in an amber bottle with minimum headspace.

Chlorine Dioxide Concentration. Chlorine dioxide solutions below 20 mg/L were too dilute to titrate accurately and quickly in order to determine the concentration. Personal communications[77] and the literature[43] indicate that absorbance and molar absorptivity are normally used to determine the concentration.

The spectrum of ClO_2 contains a very broad peak between 349 and 369 nm. The maximum was found to be 359 nm (the literature values vary from 355 to 365 nm). The reported values for the molar absorptivity of ClO_2 in water vary from 1,000 to 1,260 M^{-1} cm^{-1}.[78] The median of 1,190 was used for this study. The concentration of each sample was determined using Beer's Law: $A = \varepsilon bc$. Multiplying the concentration in moles/liter by 67,450 mg/mole gives milligrams/liter.

To insure that the observed absorbance and the molar absorptivity could be used to determine the concentration accurately, the following test was performed. A 10-mL ClO_2 sample was titrated with 0.0101 N sodium thiosulfate (using Thyodene indicator) to determine the concentration. This starch-iodide titration was carried out at pH 7 rather than pH 4. The ClO_2 reaction involves a 1-electron shift at pH 7; there is a 5-electron shift at pH 4. Therefore, five times as much thiosulfate would have been required at pH 4. The solution was buffered at pH 7 with a phosphate buffer prepared as described in Standard Methods.[79] Five milliliters of the buffer were used. The absorption of the chlorine dioxide at 359 nm was determined, and the molar absorptivity, calculated by use of Beer's Law, was found to be 1,255 M^{-1} cm^{-1}. This value agrees with the literature. This molar absorptivity was not used in the calculations because only one experiment was performed to insure that it was within the literature values.

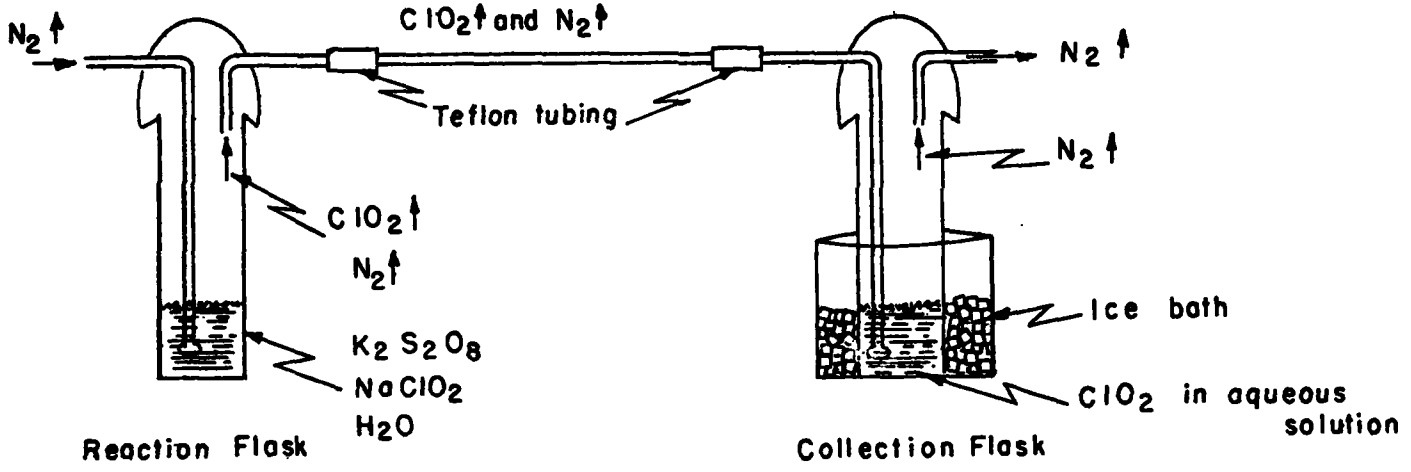


Figure 2. Experimental Apparatus for the Preparation of Chlorine Dioxide.

RESULTS AND DISCUSSION

Introduction

This study has developed methods for the determination of the oxidants bromine, monobromamine, chlorine dioxide, and iodine in aqueous solutions. These methods rely on the reaction of the oxidant with syringaldazine at neutral pH to give a colored product. The absorbance (λ_{max} = 530 nm) of the product is proportional to the concentration of the oxidant.

The approach for developing the colorimetric methods involved determining:

1. Whether the oxidant reacted quantitatively with syringaldazine under conditions developed for chlorine (FACTS II); if not, a modified FACTS II procedure that would be quantitative must be developed.

2. The concentration range over which Beer's Law would apply for each variant procedure.

3. The extent of fading, if any, associated with each variant procedure.

4. The lower limit of detection for each variant procedure.

5. The stoichiometry of the reaction between the oxidant and syringaldazine for the procedure finally adopted.

Bromine and Monobromamine

Procedure Development. Initially, both bromine and monobromamine were allowed to react with syringaldazine under conditions of the FACTS II procedure developed for chlorine.[70] When aqueous solutions of bromine reacted directly with syringaldazine, a colored product was produced rapidly. When aqueous solutions of monobromamine reacted with syringaldazine, the colored product formed at a much slower rate; the absorbance of the product from the reaction of various concentrations of monobromamine increased throughout the 5-minute reaction. Thus, the syringaldazine method did not differentiate absolutely between free bromine and monobromamine. To obtain a satisfactory test for total bromine, a modified FACTS procedure was necessary, because the FACTS II procedure did not provide acceptable results for monobromamine.

To insure a rapid quantitative measure of total bromine, the FACTS II procedure was modified to include the addition of potassium iodide (KI) prior to the addition of indicator. The modified procedure developed for total bromine was as follows:

1. A 5-mL sample of the solution to be tested (aqueous bromine or monobromamine) was pipetted into a 10-cm test tube.

2. Two-tenths milliliter of FACTS II buffer was added.

3. Various amounts of solid KI were added. Three different amounts were tested: ∿3 mg (three or four crystals), ∿9 to 18 mg, and ∿60 mg.

4. The tube was capped and inverted several times to insure complete dissolution of the KI.

5. Two milliliters of syringaldazine indicator solution (118 mg/L in 2-propanol) were added, and the tube was capped and inverted twice to mix.

6. The absorbance of the solution at 530 nm was determined with a spectrophotometer. The readings were taken after 1 minute with the use of a cuvette of appropriate path length. All readings were normalized to a 1-cm path length for the purpose of recording.

The three different amounts of KI gave quite different results with bromine than with monobromamine. The results are presented in Figures 3 through 6.

Figure 3 shows the results of using the different amounts of KI after a 1-minute reaction of bromine with syringaldazine, in accordance with the modified procedure. The raw data are tabulated in Table A-1 of Appendix A, which includes additional points of higher bromine concentrations not shown in Figure 3.

The medium amount of KI (10 to 18 mg) produced results that gave a better line than that produced by 60 mg of KI. The line was much closer to the intercept and the points described by the line were closer to the line (the correlation coefficient was higher). The amount of color produced by the large amount of KI alone was no more than one-half absorbance unit higher than the amount produced by the medium amount.

Figure 4 shows the results of the different amounts of KI at the maximum absorbance observed in the reaction of bromine with syringaldazine in accordance with the modified procedure.

Figure 5 shows the results of the different amounts of KI after a 1-minute reaction of monobromamine with syringaldazine in accordance with the modified procedure. The raw data are tabulated in Table A-2 of Appendix A, which includes data not shown in the figure.

Figure 6 shows the results of the different amounts of KI at the maximum absorbance observed in the reaction of monobromamine with syringaldazine in accordance with the modified procedure.

Whereas there was a marked difference in the results obtained with different amounts of KI when determining bromine, this difference was not as noticeable in the determination of monobromamine. That the lines obtained for the regression did not go through or near zero might have been caused by fading of the product, which is discussed later. Experiments were conducted according to the above procedure to analyze aqueous solutions of bromine and monobromamine at the three different levels of KI concentration.

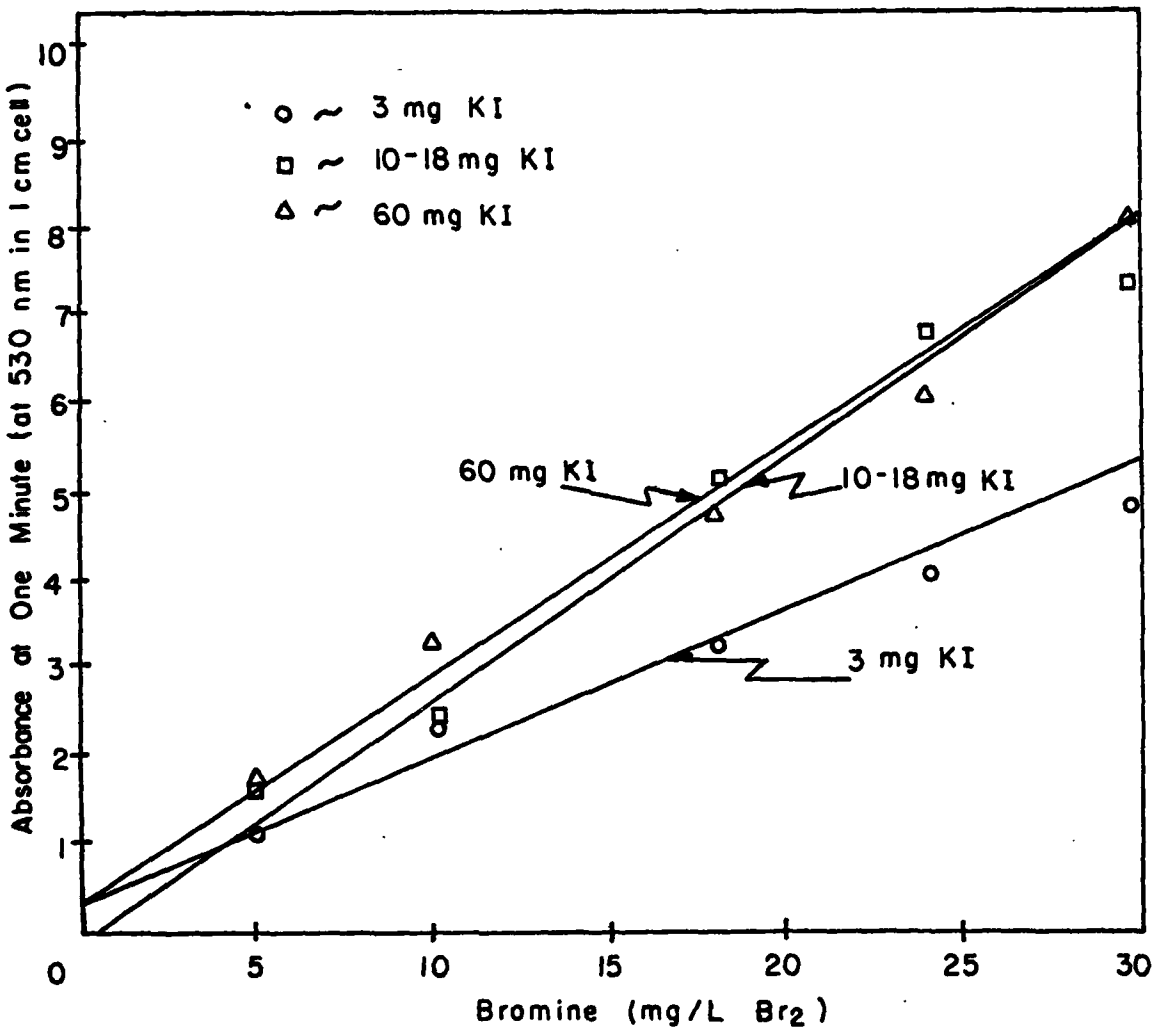


Figure 3. Comparison of the Absorbance at 1 Minute of Various Concentrations of Bromine Exposed to Three Levels of Potassium Iodide in the Modified FACTS II Procedure.

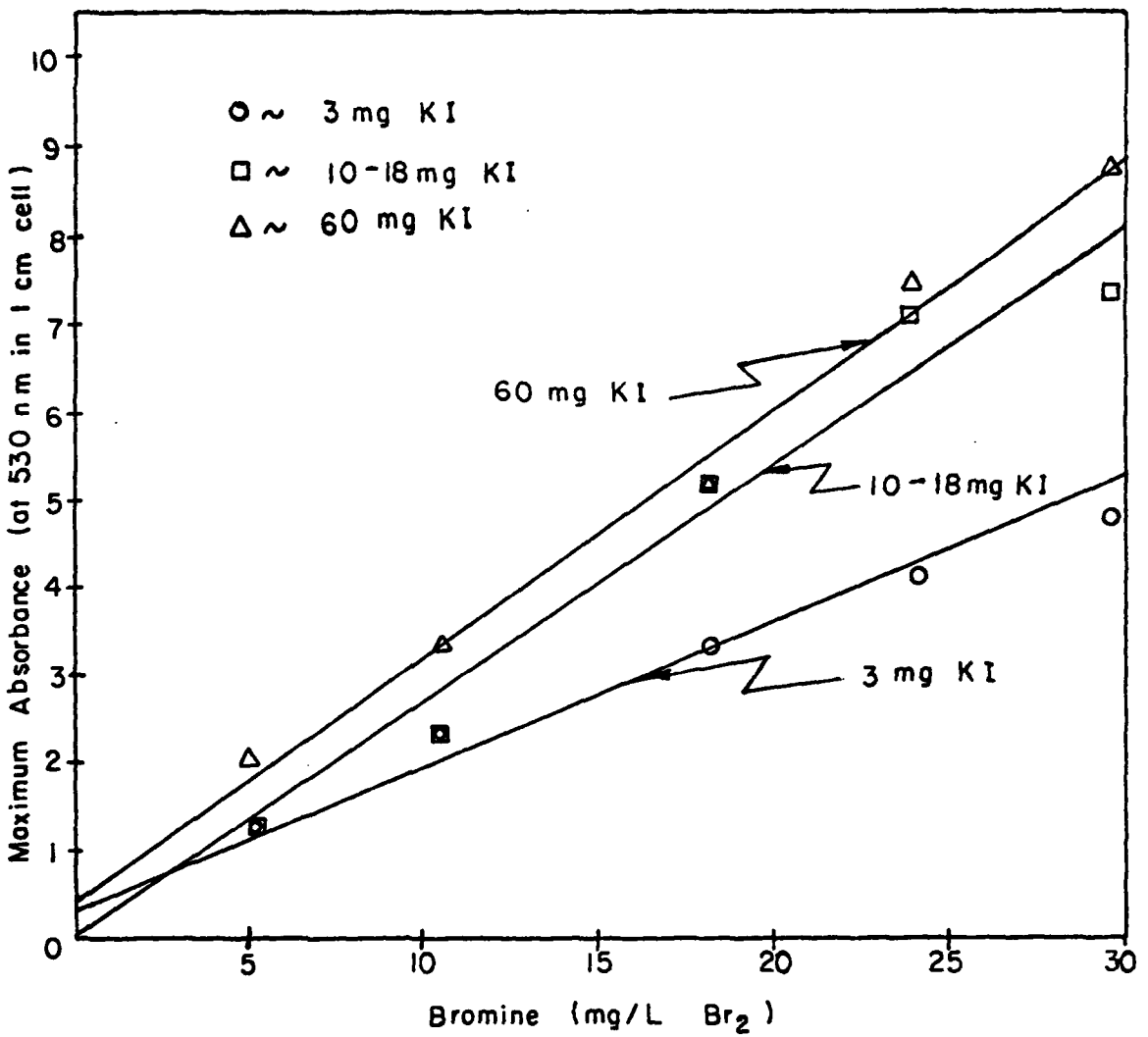


Figure 4. Comparison of the Maximum Absorbance of Various Concentrations of Bromine Exposed to Three Levels of Potassium Iodide in the Modified FACTS II Procedure.

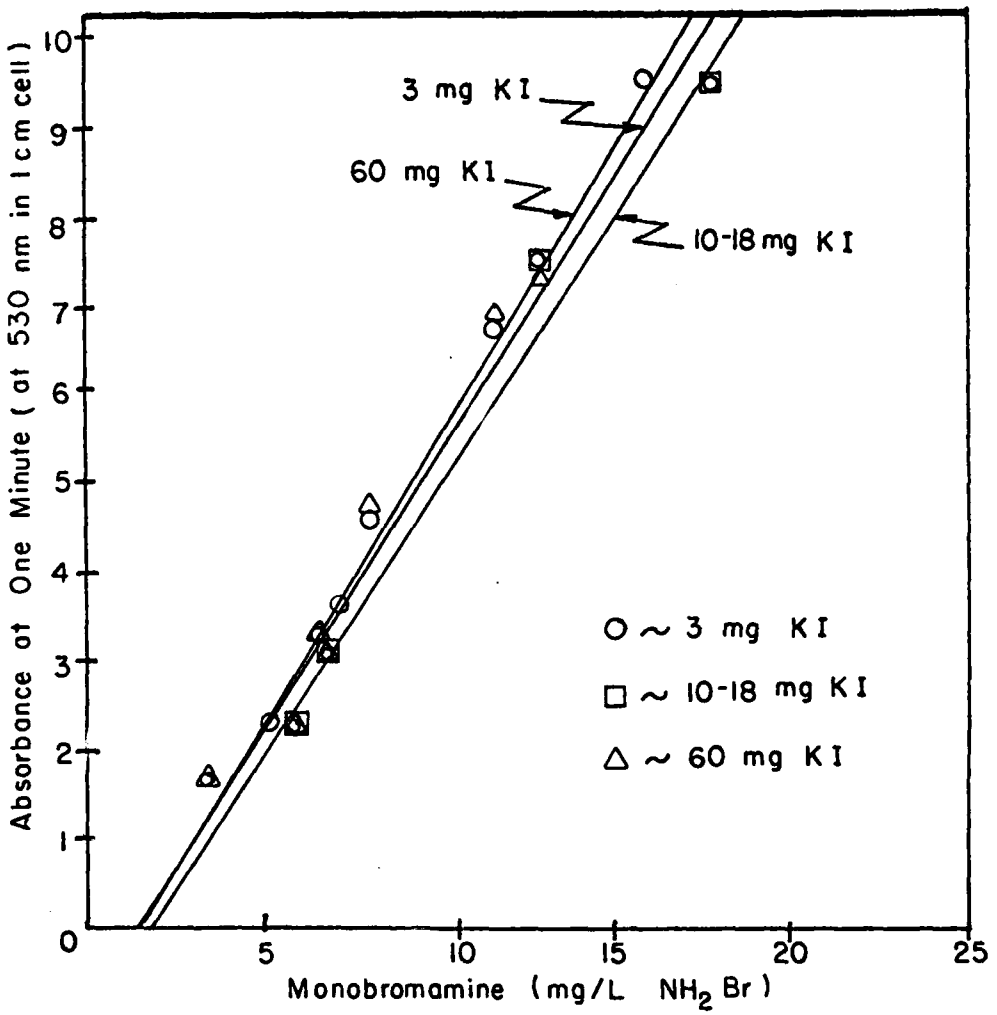


Figure 5. Comparison of the Absorbance at 1 Minute of Various Concentrations of Monobromamine Exposed to Three Levels of Potassium Iodide in the Modified FACTS II Procedure.

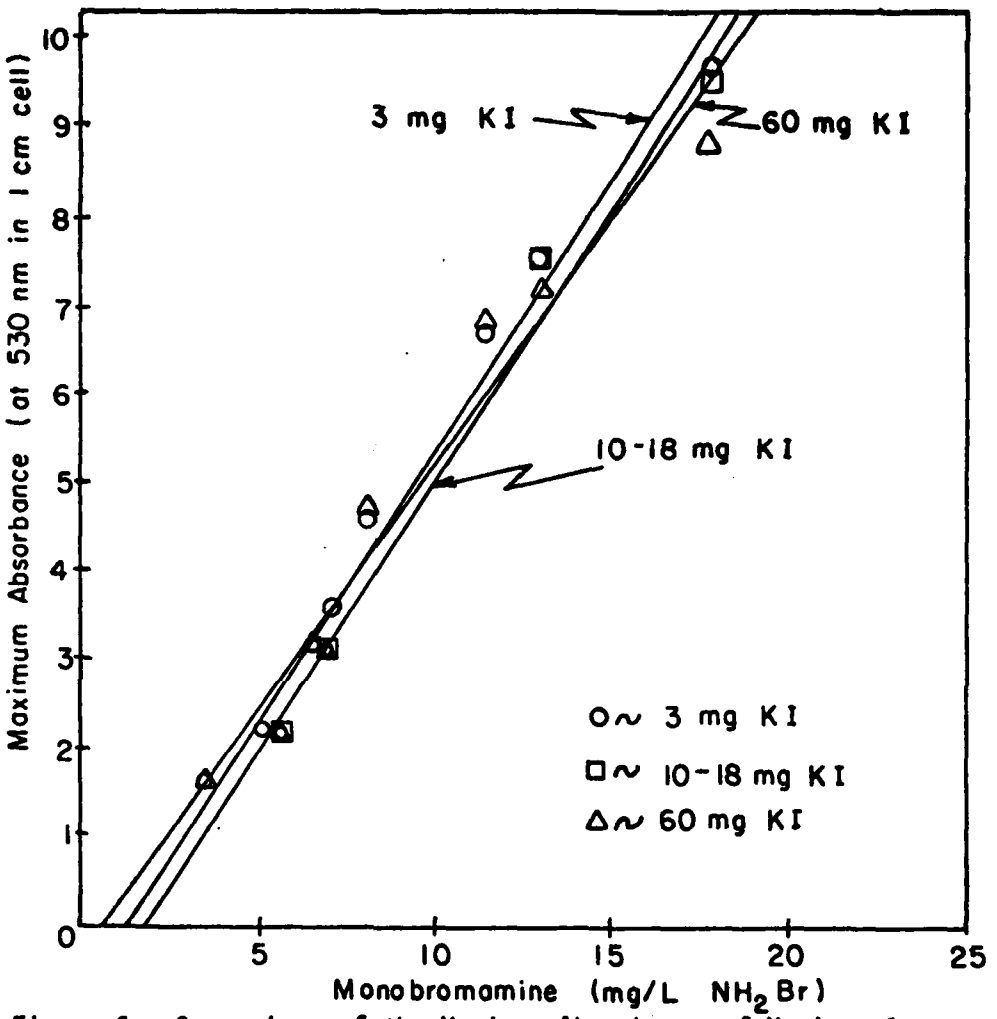


Figure 6. Comparison of the Maximum Absorbance of Various Concentrations of Monobromamine Exposed to Three Levels of Potassium Iodide in the Modified FACTS II Procedure.

Concentration Range. Varying concentrations of bromine and monobromamine were prepared in CDFW. These solutions were used to determine the absorbance at 530 nm of the colored product according to both the FACTS II procedure and the modified FACTS II procedure. The results are shown graphically in Figures 7 through 10.

Figure 7 shows the results of the reaction of various concentrations of bromine with use of the FACTS II procedure. The absorbance for each sample is the observation after a 1-minute reaction of bromine with syringaldazine in accordance with the FACTS II procedure. The raw data are tabulated in Table A-3 of Appendix A. Additional data points are included for higher values of bromine, which were used to develop the linear regression of the line describing points in the plateau after the equivalence point.

Figure 8 shows the results for the reaction of various concentrations of bromine with the modified FACTS II procedure. A comparison of Figures 7 and 8 shows very little difference in the reaction of bromine in the FACTS II and modified FACTS II procedures. The slopes are almost the same: 0.264 with FACTS II and 0.268 with the modified FACTS II procedure. The modified procedure did bring the intercept closer to the origin; this may have resulted from color stabilization when KI was added. The raw data are tabulated in Table A-1 of Appendix A.

In order to evaluate the daily reproducibility of both procedures, equations of the lines were determined for each day's data (Table 2). All data from all the days were used in determining the best fit for the combined line.

Figure 9 shows the results of the reaction of various concentrations of monobromamine with the FACTS II procedure. The absorbance for each sample is the maximum observation during the 5-minute reaction period of monobromamine with syringaldazine in accordance with the FACTS II procedure. These observations were taken at the 4- or 5-minute point because color did not develop fully until then. The raw data are tabulated in Table A-4 of Appendix A. Additional data points are included for higher values of monobromamine. These data were used in developing the linear regression for the line describing points in the plateau after the equivalence point.

Figure 10 shows the results of the reaction of various concentrations of monobromamine with the modified FACTS II procedure. The absorbance for each sample is the 1-minute point because color developed quickly. A comparison of Figures 9 and 10 demonstrates that the modified procedure produced more color (shown by the larger slope) and brought the intercept closer to the origin. In order to evaluate the daily reproducibility of the procedures, equations of the lines were determined for each day's data (Table 3). All data from all the days were used in determining the combined lines. The raw data are tabulated in Table A-2 of Appendix A. Additional data points are included for higher values of monobromamine. These data were used to develop the linear regression for the line describing points in the plateau after the equivalence point.

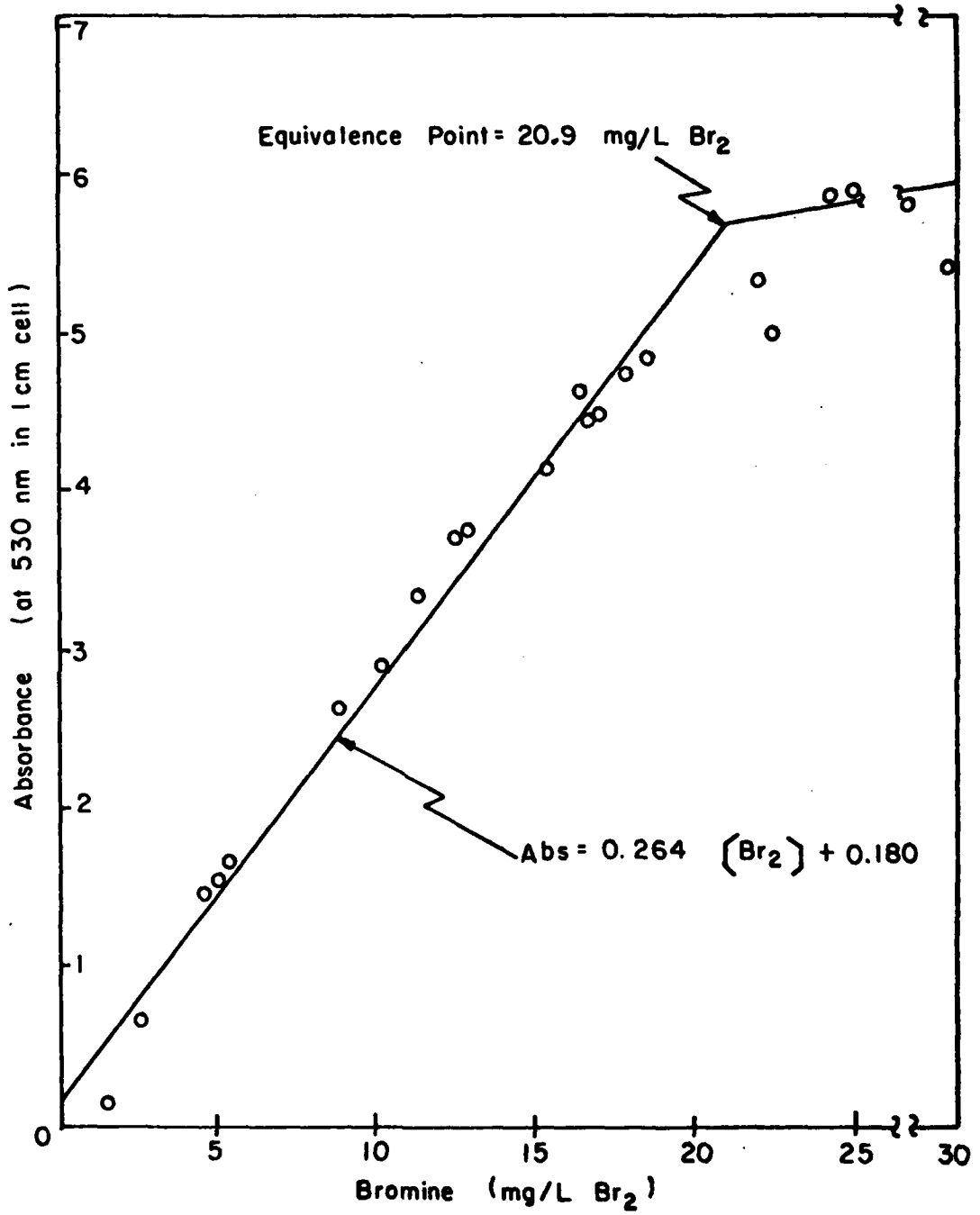


Figure 7. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Bromine and Syringaldazine in the FACTS II Procedure.

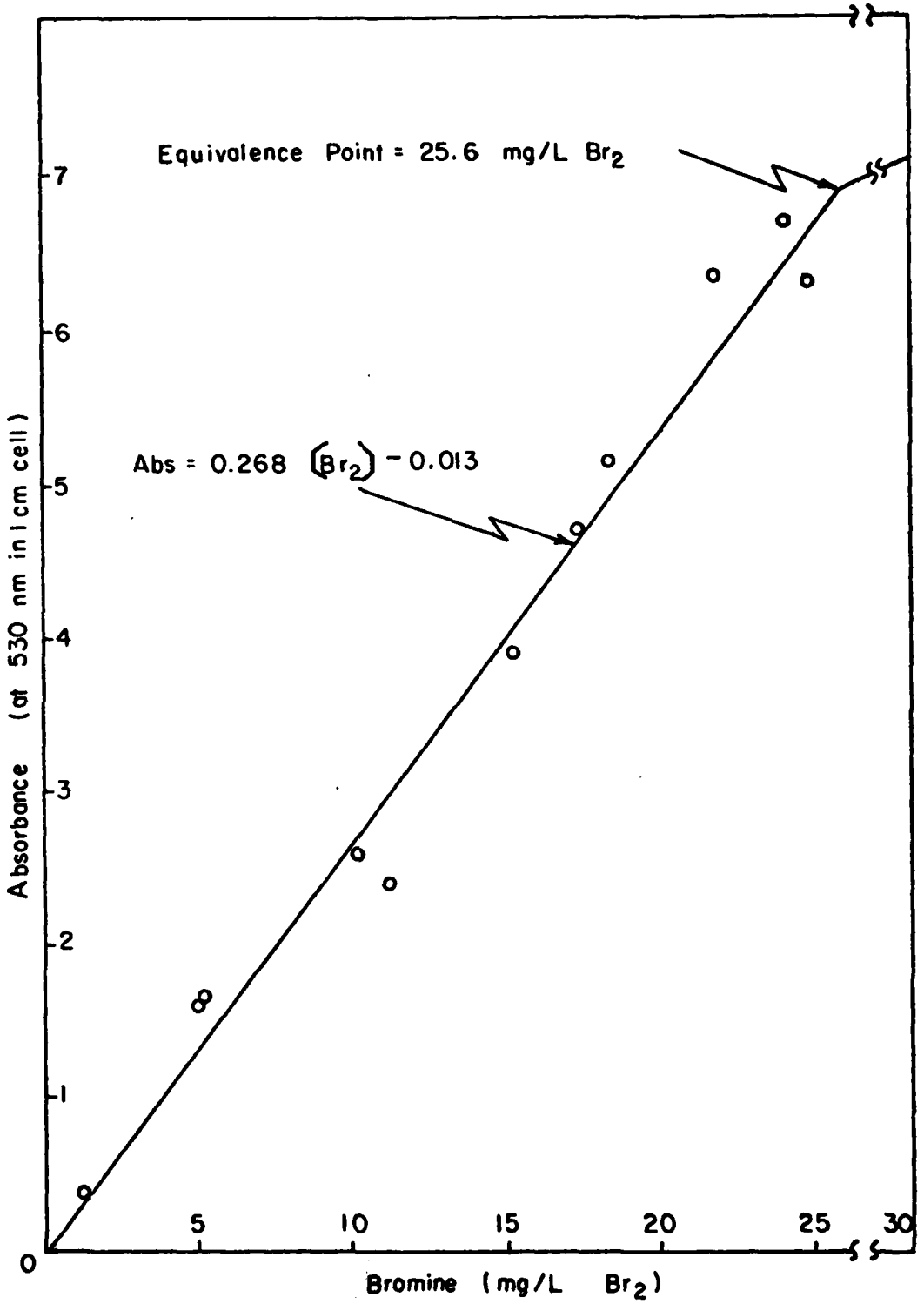


Figure 8. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Bromine and Syringaldazine in the Modified FACTS II Procedure.

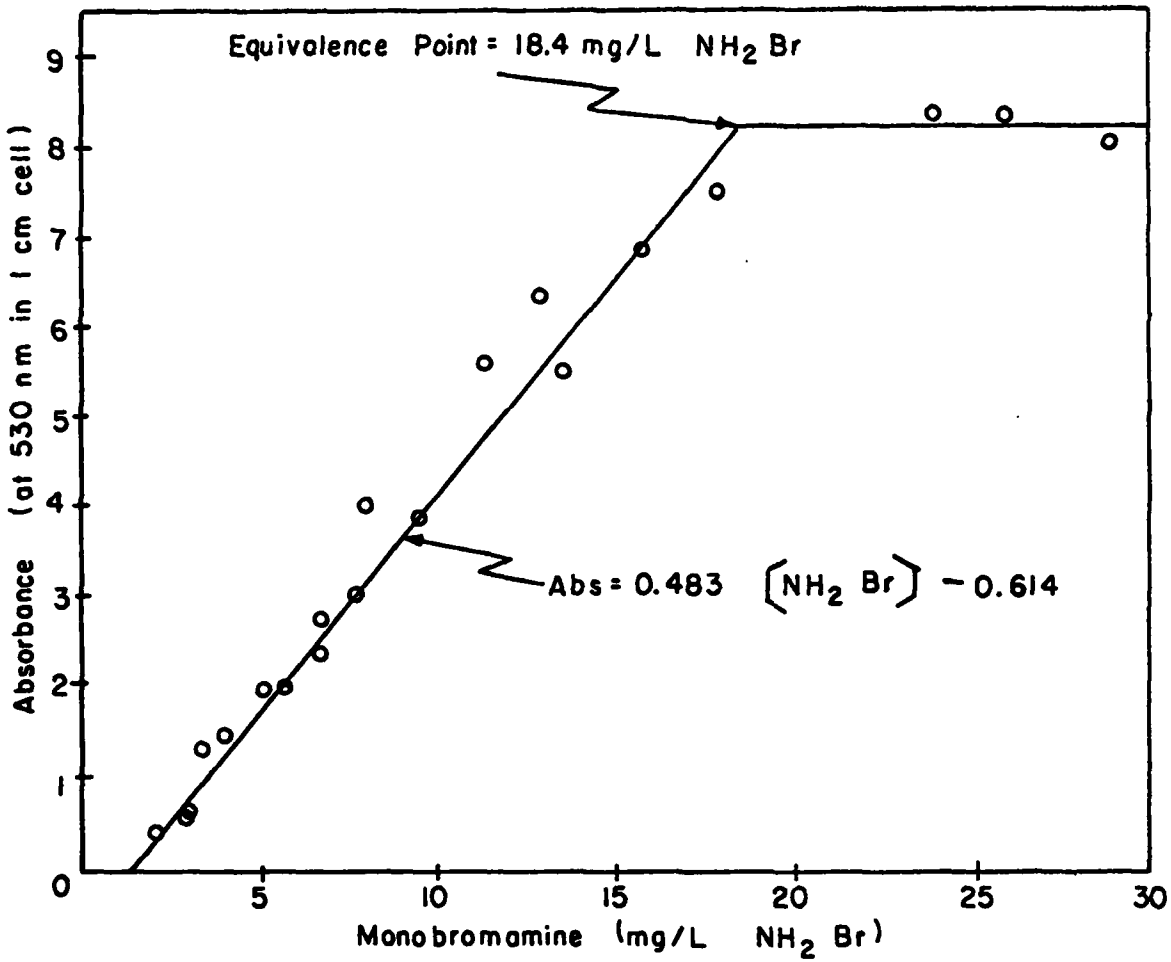


Figure 9. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Monobromamine and Syringaldazine in the FACTS II Procedure.

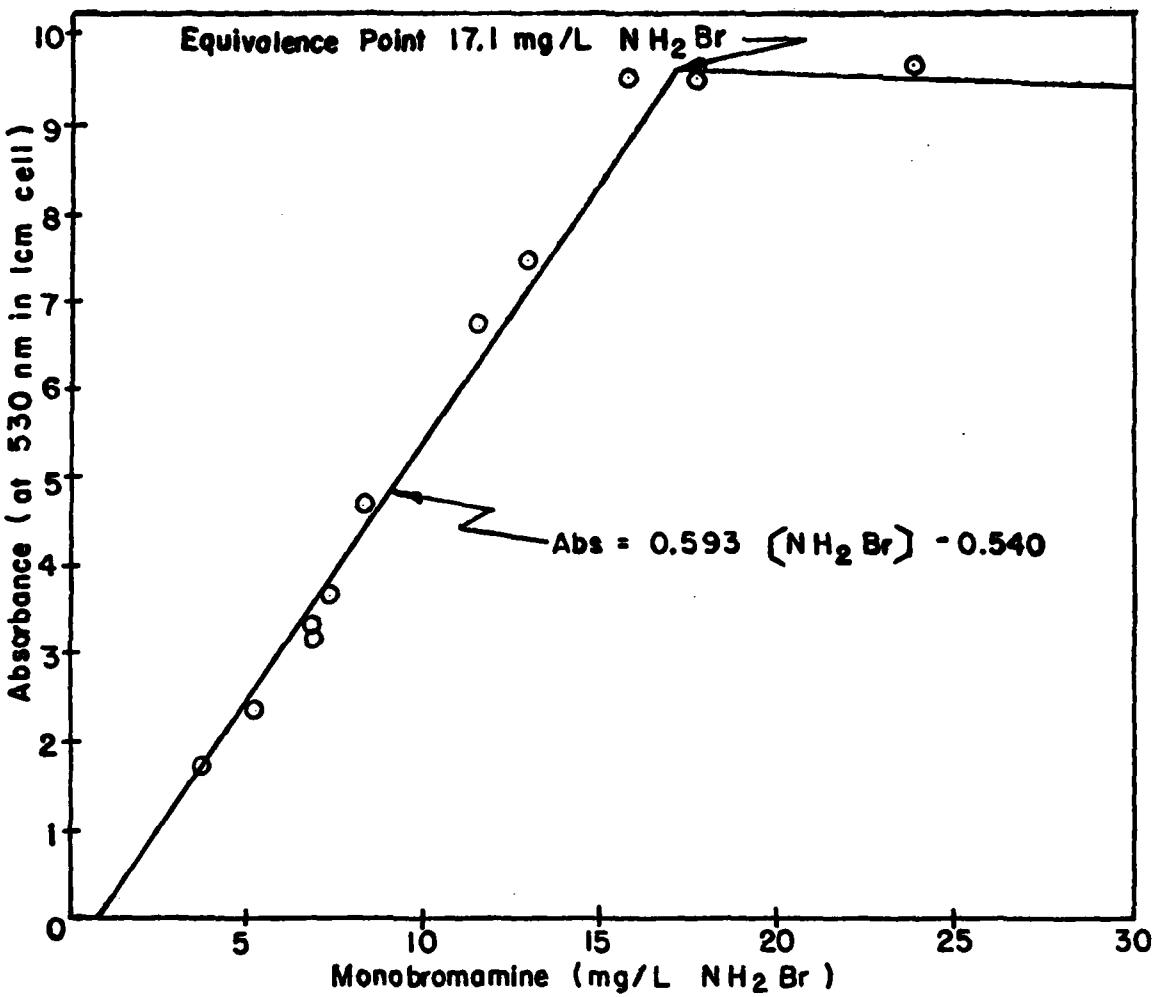


Figure 10. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Monobromamine and Syringaldazine in the Modified FACTS II Procedure.

TABLE 2. EQUATIONS OF THE LINES OBTAINED FROM A LINEAR REGRESSION OF THE DATA FOR THE REACTION BETWEEN BROMINE AND SYRINGALDAZINE[a]

Date	Equation
FACTS II Procedure	
7 September 1977	Abs = 0.237 $[Br_2]$ + 0.579
9 September 1977	Abs = 0.277 $[Br_2]$ + 0.140
19 September 1978	Abs = 0.273 $[Br_2]$ - 0.037
25 February 1978	Abs = 0.244 $[Br_2]$ + 0.416
Combined	Abs = 0.264 $[Br_2]$ + 0.180
Modified FACTS II Procedure[b]	
19 February 1978	Abs = 0.271 $[Br_2]$ - 0.019
25 February 1978	Abs = 0.264 $[Br_2]$ - 0.013
Combined	Abs = 0.268 $[Br_2]$ - 0.013

a. $[Br_2]$ in mg/L.

b. Ten to 18 mg of KI were used in each experiment.

The linear regression of the data obtained for the monobromamine did not go near zero, which may result from the pH used in determining the monobromamine. It has been shown that pH affects the stability of the colored product. Monobromamine was prepared at a pH of 8; if the buffer system used was not strong enough to overcome the high pH, this could have caused fading of the product and, therefore, an intercept of less than zero. This pattern is not consistent with the slow color development noted for the unmodified procedure. However, because no pH measurements were taken, a low pH remains a possible explanation.

Aqueous solutions of bromine, when determined by the FACTS II procedure, obeyed Beer's Law through 21 mg/L, which is 1.31×10^{-4} M. When KI was added, the range through which Beer's Law was obeyed was 26 mg/L, which is 1.63×10^{-4} M. Aqueous solutions of monobromamine, when determined by the FACTS II procedure, obeyed Beer's Law through 19 mg/L as NH_2Br, which is 1.98×10^{-4} M. When KI was added, the range through which Beer's Law was obeyed was up to 18 mg/L as NH_2Br, which is 1.88×10^{-4} M.

TABLE 3. EQUATIONS OF THE LINES OBTAINED FROM A LINEAR REGRESSION OF THE DATA FOR THE REACTION BETWEEN MONOBROMAMINE AND SYRINGALDAZINE[a]

Date	Equation
FACTS II Procedure	
29 January 1978	Abs = 0.473 [NH_2Br] - 0.759
4 February 1978	Abs = 0.483 [NH_2Br] - 0.735
14 February 1978	Abs = 0.462 [NH_2Br] - 0.407
26 February 1978	Abs = 0.466 [NH_2Br] - 0.380
18 March 1978	Abs = 0.572 [NH_2Br] - 0.942
Combined	Abs = 0.483 [NH_2Br] - 0.614
Modified FACTS II Procedure[b]	
14 February 1978	Abs = 0.693 [NH_2Br] - 1.32
26 February 1978	Abs = 0.593 [NH_2Br] - 0.711
18 March 1978	Abs = 0.655 [NH_2Br] - 0.800
Combined	Abs = 0.593 [NH_2Br] - 0.540

a. [NH_2Br] in mg/L.

b. Equations utilized experiments employing all KI additions (3 mg, 10 to 18 mg, 60 mg).

Fading. To develop a procedure for aqueous solutions of bromine, the fading of the colored product must be minimized. Fading occurred in previous studies that used the FACTS II procedure to determine chlorine. Therefore, experiments were undertaken to determine the extent of fading with the FACTS II and modified FACTS II procedures for various concentrations of bromine.

The rates of fading of the product of reaction between bromine and syringaldazine in the FACTS II procedure are shown in Figure 11. (The color had developed fully in the first minute.) For lower concentrations, fading was negligible. At the higher concentrations of bromine (>17 mg/L), some fading occurred.

The addition of KI in the modified FACTS II procedure seemed to stabilize the color (Fig. 12). The reason for this stabilizing effect has not been determined. The data for these experiments are tabulated in Tables A-5 and A-6 of Appendix A.

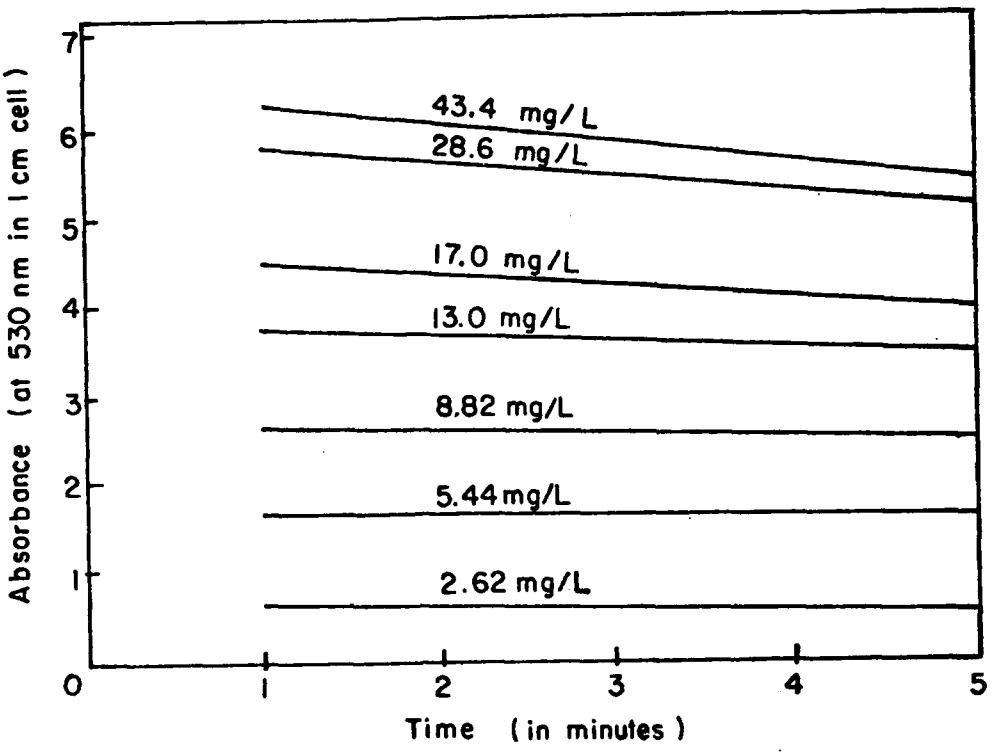


Figure 11. Color Fading in the FACTS II Procedure for Bromine.

The FACTS II procedure is considered an unacceptable procedure for determining monobromamine, in view of the slow color development (Fig. 13). The addition of KI accelerated the reaction to yield maximum color within 1 minute, and that color was maintained (within one-half absorbance unit) for most of the 5-minute period (Fig. 14). Data are tabulated in Table A-7 of Appendix A for the FACTS II Procedure and in Table A-8 for the modified FACTS II procedure.

Lower Limit of Detection. No direct attempt was made to determine the lower limit of detection for either bromine or monobromamine. However, good results were obtained down to 1.48 mg/L bromine and down to 2.00 mg/L monobromamine. If 0.1 were accepted as the lowest readily observed (with the spectrophotometer) absorbance value, then the lower limit of detection for bromine would be 0.4 mg/L, and the lower limit of detection for monobromamine would be 1.1 mg/L as NH_2Br.

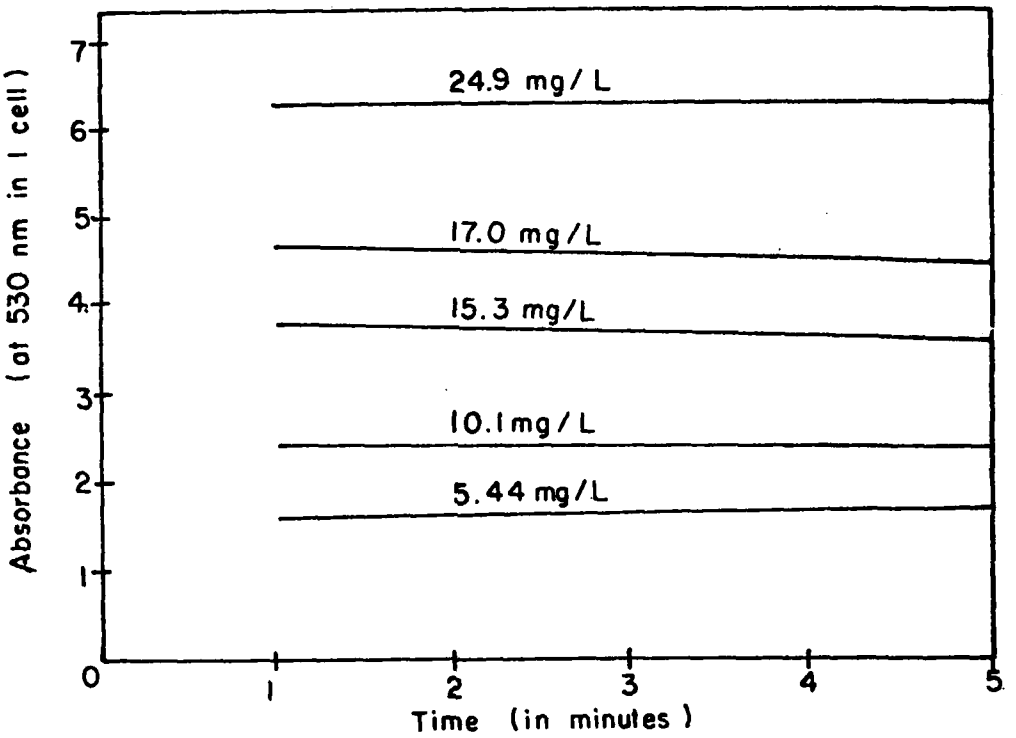


Figure 12. Color Fading in the Modified FACTS II Procedure for Bromine (10 to 18 mg KI).

Stoichiometry. The Beer's Law plots (Figs. 7-10) show the results of what are effectively spectrophotometric titrations of aqueous solutions of bromine and monobromamine with the FACTS II and the modified FACTS II procedures. The stoichiometry of the reaction was determined by the mole ratio of bromine or monobromamine to syringaldazine required for maximum color development. These mole ratios were determined from the ratios observed at the intercepts of the two straight lines in each curve. The intercept of the two lines is the equivalence point: the point at which the molar concentrations of the oxidant and syringaldazine are equal. The equivalence point is determined by solving the simultaneous equations for the concentration of Br_2 or NH_2Br, as the case may be. The equations used were those that describe the Beer's Law portion of the plot and the plateau region.

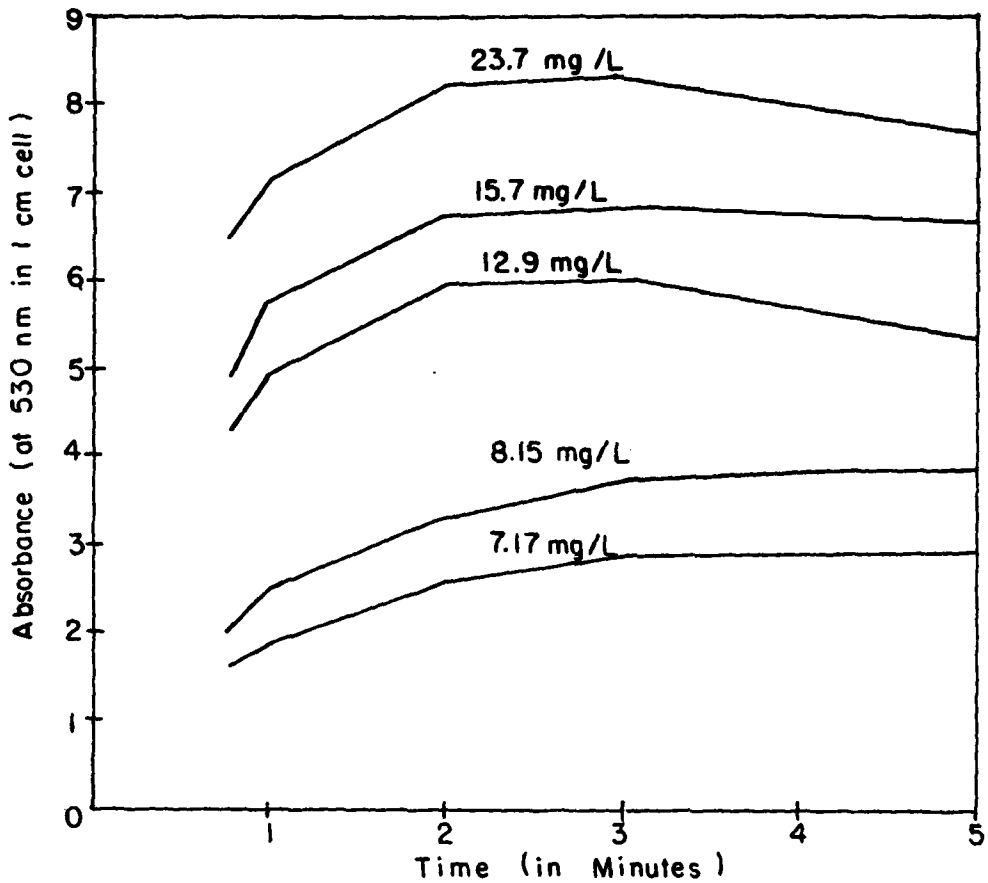


Figure 13. Color Development in the FACTS II Procedure for Monobromamine.

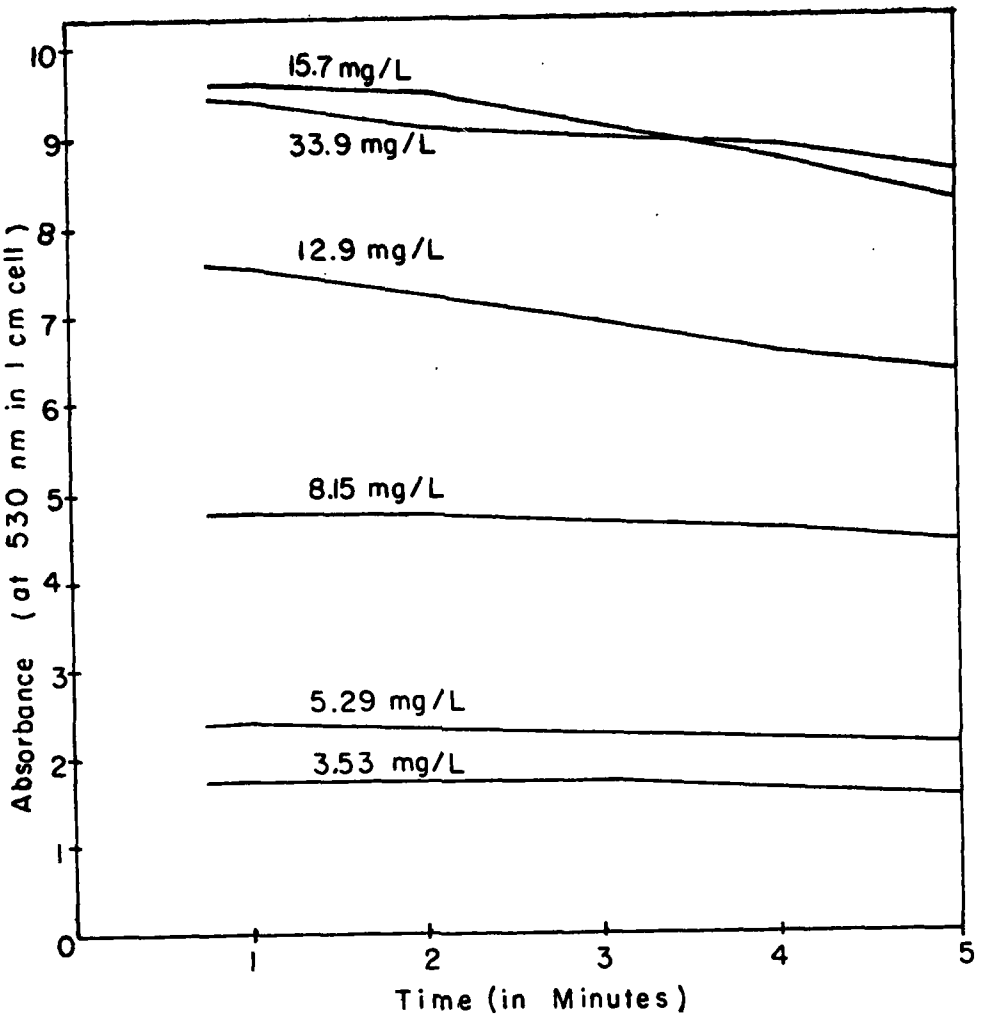


Figure 14. Color Development and Fading in the Modified FACTS II Procedure for Monobromamine (3 mg KI).

The equivalence points and molar ratios are shown in Tables 4 and 5. The mole ratio is determined by the following sample calculation:

$$\text{Moles } Br_2 = \frac{\text{equivalence point x (g/L) volume of } Br_2 \text{ solution (liters)}}{\text{molecular weight of } Br_2 \text{ (g/mole)}}$$

$$\text{Moles Syringaldazine} = \frac{\text{indicator solution concentration x (g/L) volume (liters)}}{\text{molecular weight of syringaldazine (g/mole)}}$$

From Table 4

$$\text{Moles } Br_2 = \frac{0.0209 \text{ g/L} \times 0.005 \text{ L}}{159.8 \text{ g/mole}} = 6.539 \times 10^{-7} \text{ mole}$$

$$\text{Moles Syringaldazine} = \frac{0.118 \text{ g/L} \times 0.002 \text{ L}}{360.4 \text{ g/mole}} = 6.548 \times 10^{-7} \text{ mole}$$

$$\text{Mole Ratio} = \frac{\text{Moles } Br_2}{\text{Moles Syringaldazine}} = 0.9986 \approx 1.00$$

The data in Table 4 indicate that the ratio of bromine to syringaldazine in the FACTS II procedure is approximately 1 mole of bromine per mole of syringaldazine. With the modified procedure, the ratio is approximately 1.2 mole of bromine to 1 mole of syringaldazine. The reason for the ratio change is not known.

TABLE 4. EQUIVALENCE POINTS FOR THE REACTION BETWEEN BROMINE AND SYRINGALDAZINE

Date	Equivalence Point (mg/L)	Molar Ratio Br_2:Syr
FACTS II Procedure		
7 September 1977	21.7	1.04
9 September 1977	20.0	0.96
19 February 1978	21.0	1.00
25 February 1978	21.8	1.04
Combined	20.9	1.00
Modified FACTS II Procedure		
19 February 1978	24.2	1.16
25 February 1978	26.8	1.28
Combined	25.6	1.22

TABLE 5. EQUIVALENCE POINTS FOR THE REACTION BETWEEN MONOBROMAMINE AND SYRINGALDAZINE

Date	Equivalence Point (mg/L)	Molar Ratio NH_2Br:Syr
	FACTS II Procedure	
29 January 1978	19.1	1.52
4 February 1978	18.7	1.49
14 February 1978	18.8	1.50
26 February 1978	18.6	1.48
18 March 1978	16.1	1.28
Combined	18.4	1.46
	Modified FACTS II Procedure	
14 February 1978	15.8	1.26
26 February 1978	17.4	1.38
18 March 1978	15.9	1.26
Combined	17.1	1.36

The data in Table 5 indicate that the ratio of monobromamine to syringaldazine with both the FACTS II and modified FACTS II procedures is about 1.4:1.

Organically Polluted Water. Both the FACTS II and the modified FACTS II procedures were used to analyze the samples after reaction with bromine, as described in the Methods and Materials section. The data are tabulated in Table A-9 of Appendix A.

The breakpoint phenomenon with bromine has been demonstrated.[34,80] The objective of the present experiment was to determine whether the FACTS II and modified FACTS II procedures would show the breakpoint.

A graph of bromine added versus total bromine (measured on the amperometric titrator) and absorbance (at 530 nm) observed when the modified FACTS II procedure was used shows that the patterns are similar and that the modified procedure measured bromine and bromamines in natural water (Fig. 15). An apparent breakpoint was seen at 18 mg/L added bromine, which is a mg Br:mg ammonia nitrogen ratio of 3:1. This ratio is low. The breakpoint reaction molar stoichiometry of 3 Br_2:2 NH_3[34] would suggest a value for mg Br:mg ammonia nitrogen of 8.6:1, with an even higher ratio if the water contained appreciable amounts of organic amines.

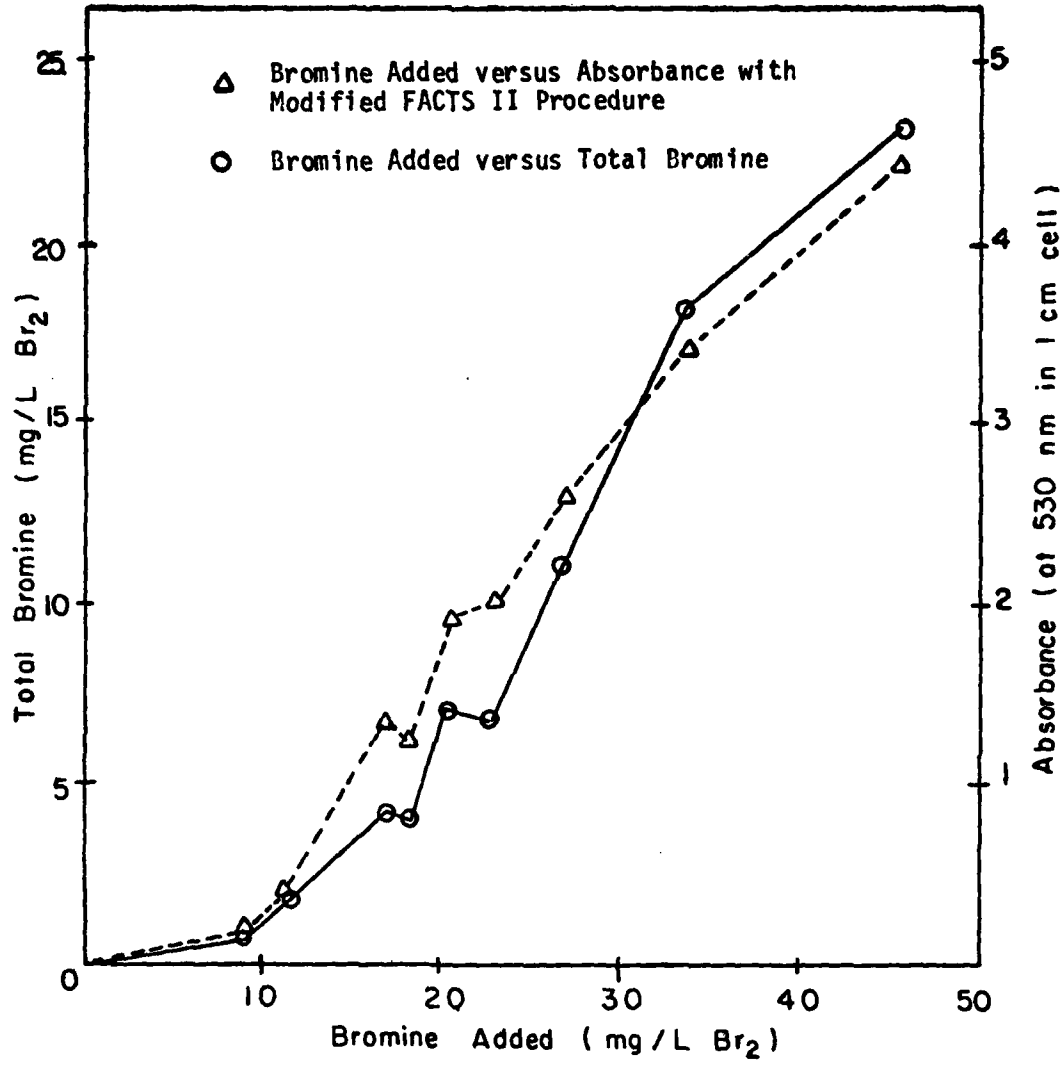


Figure 15. Comparison of Total Bromine and the Response with the Modified FACTS II Procedure for Bromine in Tests on an Organically Polluted Water Containing about 6.5 mg/L Ammonia Nitrogen.

A comparison of the FACTS II and the modified FACTS II procedures showed that the modified procedure produced much more color than the FACTS II procedure. Both procedures showed an apparent breakpoint, but that associated with the modified FACTS II procedure appeared at a lower bromine dosage (Fig. 16).

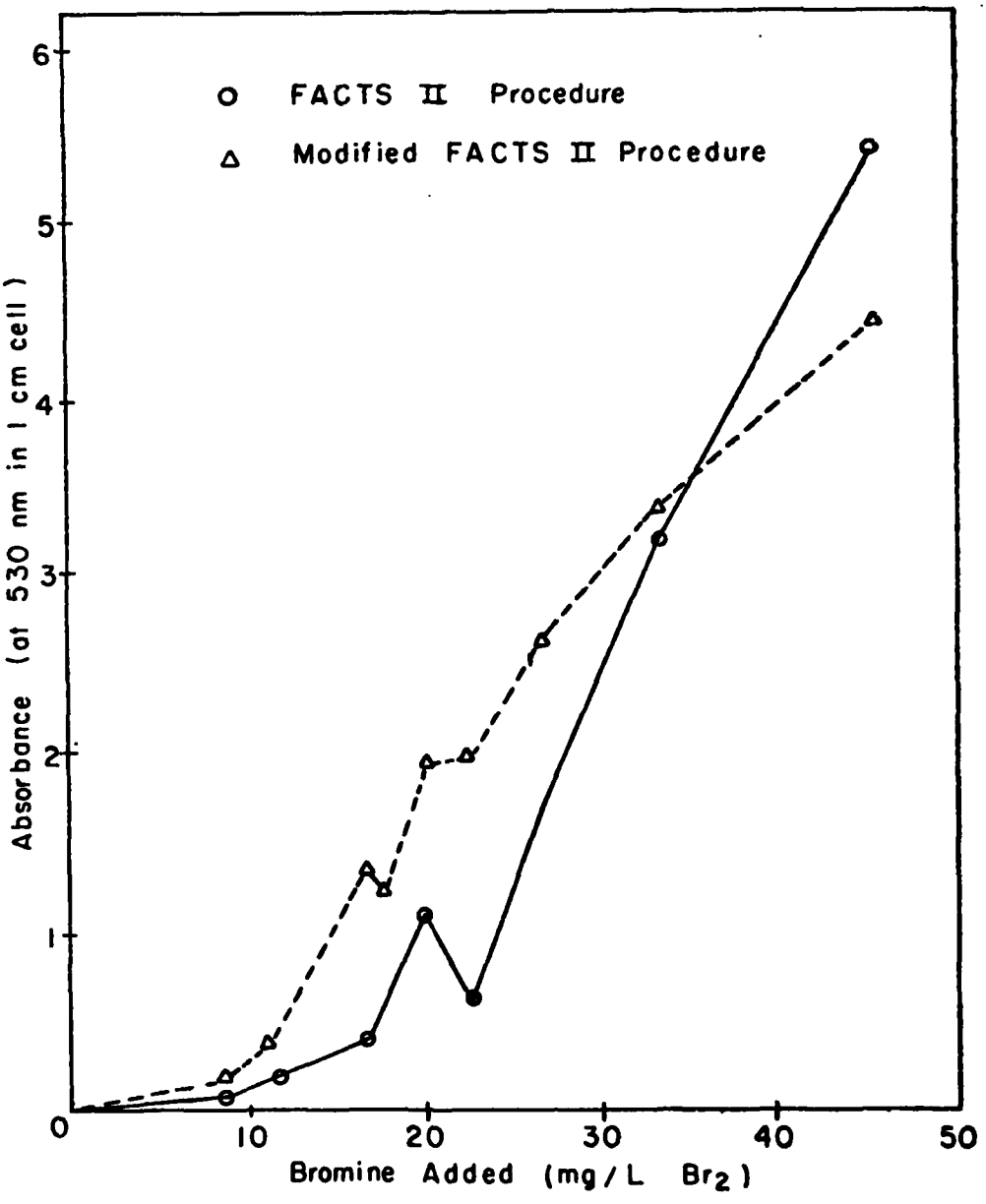


Figure 16. Comparison of the FACTS II and the Modified FACTS II Procedure for Determining Bromine in Tests on an Organically Polluted Water Containing about 6.5 mg/L Ammonia Nitrogen.

Further work should be done to determine whether the amount of color produced after the breakpoint is similar with both procedures. The reason to suppose that they should be similar is that KI addition makes very little difference with bromine (which would be present after breakpoint), but is quite important with monobromamine.

No attempt was made in this study to determine the bromine species present in the natural water.

Chlorine Dioxide

Procedure Development. Initially, chlorine dioxide was permitted to react directly with syringaldazine, as chlorine reacts in the FACTS II procedure.[70] A colored product was produced rapidly and could be measured at the 1-minute reaction time. So much fading occurred within the first minute at the higher chlorine dioxide concentrations that the absorbances were lower than when lesser amounts of chlorine dioxide were used. For this reason, the modified procedure developed for bromine and monobromamine was applied to the determination of chlorine dioxide.

Experiments using the procedure described for bromine and monobromamine were conducted with the three different amounts of KI to analyze aqueous solutions of chlorine dioxide. Unexpected results were obtained.

Figure 17 shows the results of the different amounts of KI after a 1-minute reaction of chlorine dioxide with syringaldazine in accordance with the modified FACTS II procedure. The data are tabulated in Table B-1 of Appendix B.

Figure 18 shows the results of the different amounts of KI at the maximum absorbance in the reaction of chlorine dioxide with syringaldazine in accordance with the modified FACTS II procedure. The data are tabulated in Table B-2 of Appendix B.

It can be seen that the 1-minute absorbance and the maximum absorbance associated with the addition of 3 mg KI are very similar. The similarity between the 1-minute and the maximum absorbances decreased when 10 to 18 mg KI were used. The absorbances were least comparable when 60 mg KI were used.

Concentration Range. Varying concentrations of chlorine dioxide were prepared in CDFW. These solutions were used to determine the absorbance at 530 nm of the colored product with both the FACTS II and the modified FACTS II procedures. The results are shown graphically in Figures 19 and 20.

Figure 19 shows the results of the reaction of various concentrations of chlorine dioxide with the FACTS II procedure. The absorbance for each sample is the observation after 1 minute of reaction of chlorine dioxide with syringaldazine, in accordance with the FACTS II directions. The raw

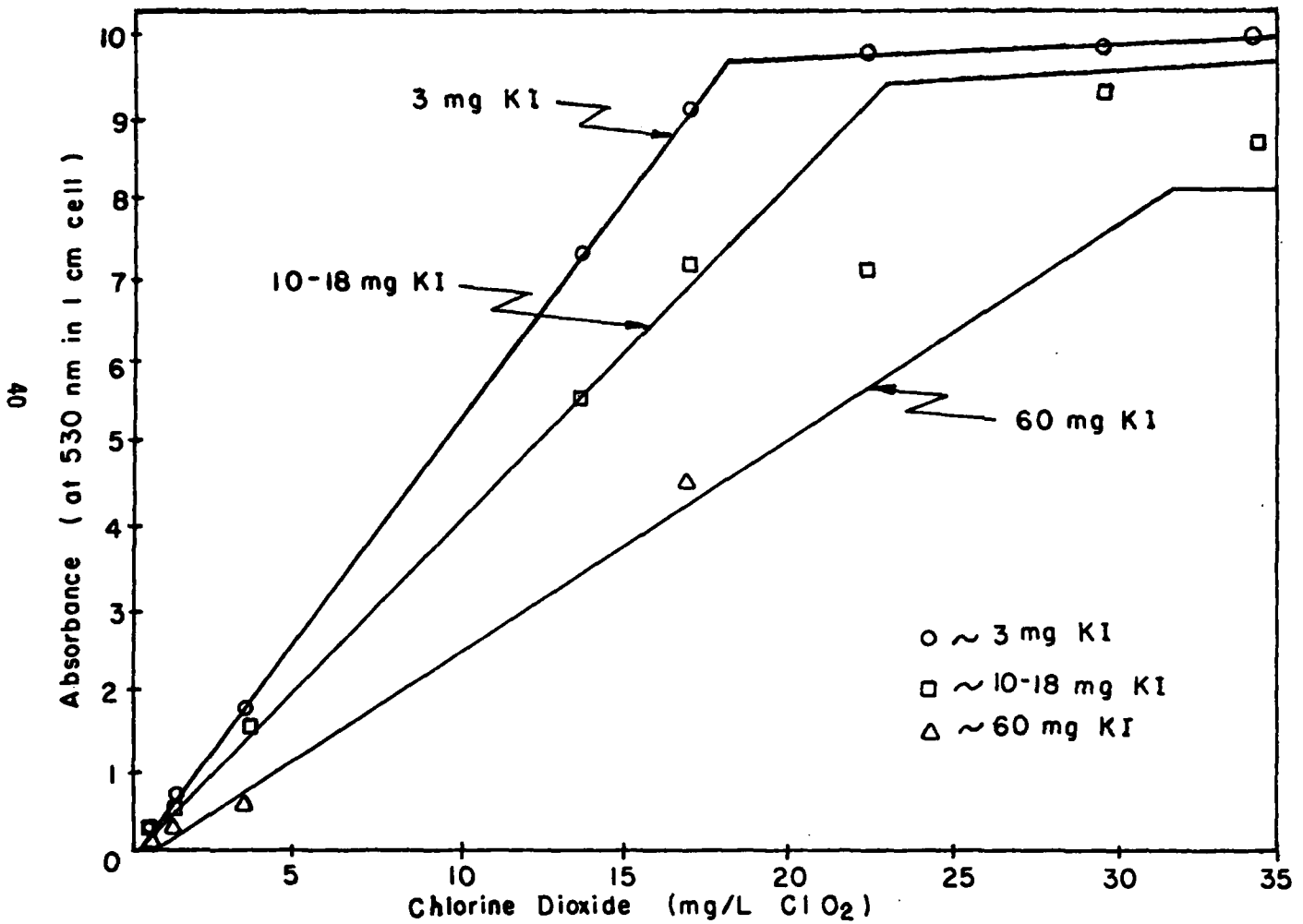


Figure 17. Comparison of the Absorbance at 1 Minute of Various Concentrations of Chlorine Dioxide Exposed to Three Levels of Potassium Iodide in the Modified FACTS II Procedure.

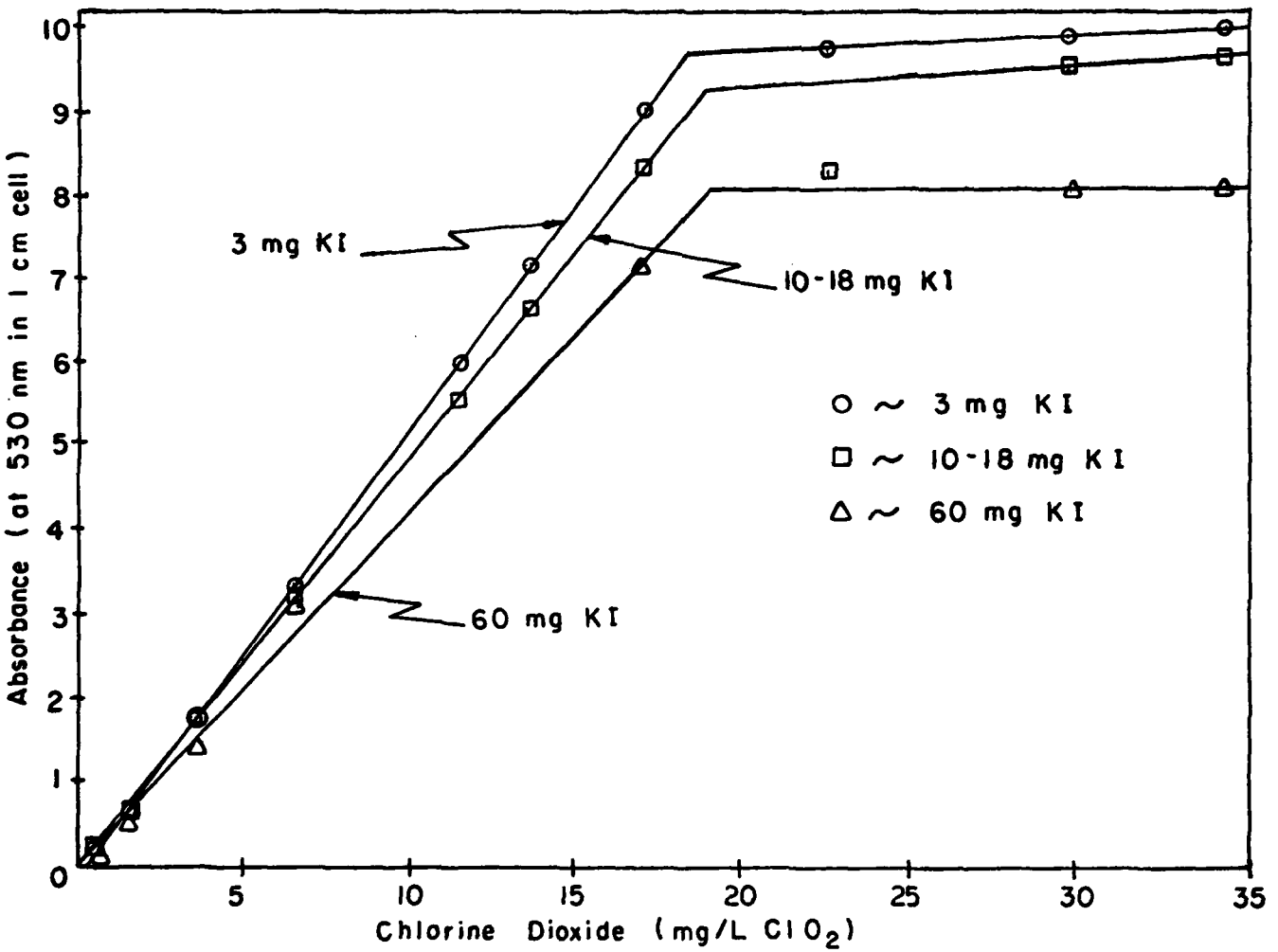


Figure 18. Comparison of the Maximum Absorbance of Various Concentrations of Chlorine Dioxide Exposed to Three Levels of Potassium Iodide in the Modified FACTS II Procedure.

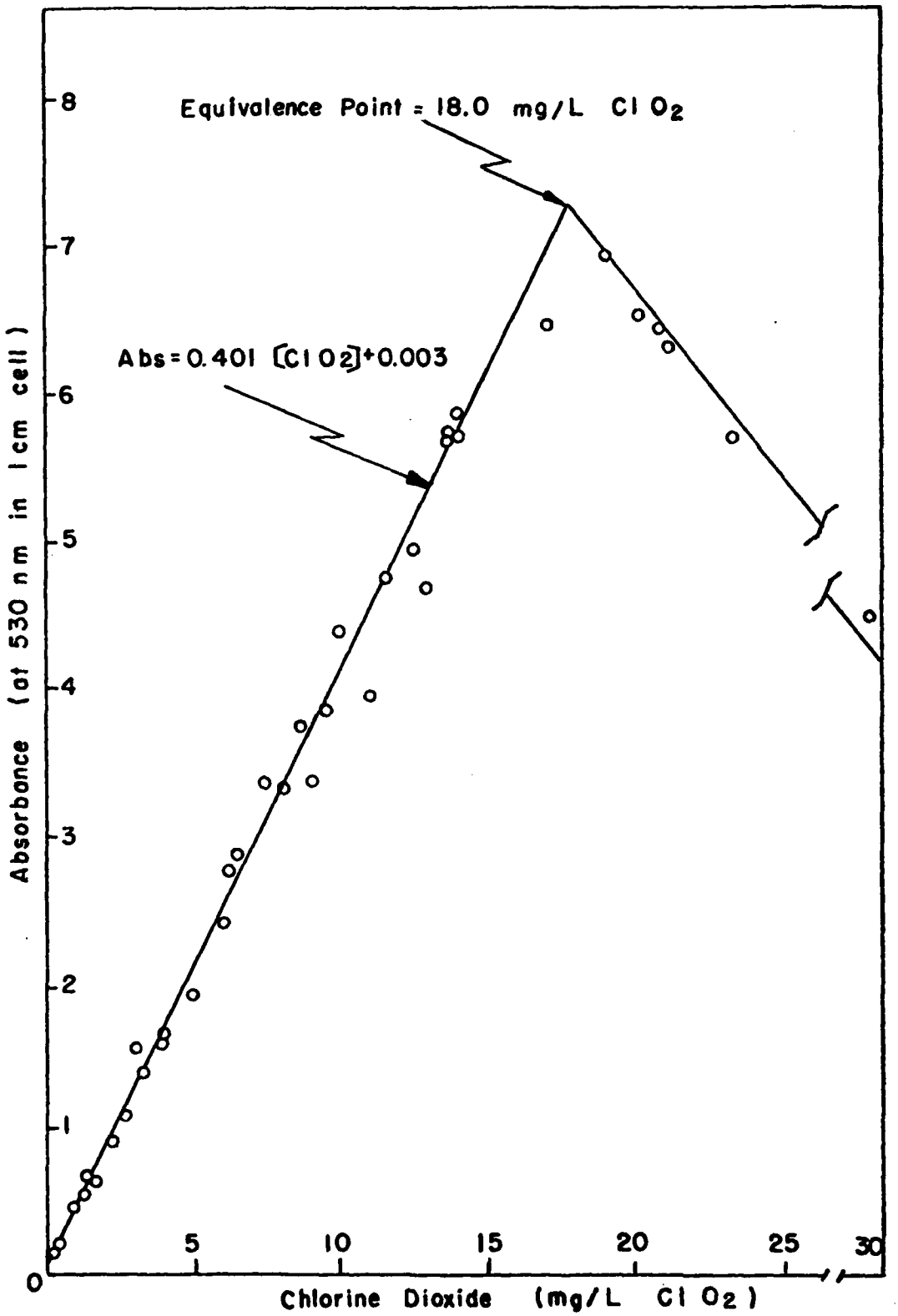


Figure 19. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Chlorine Dioxide and Syringaldazine in the FACTS II Procedure.

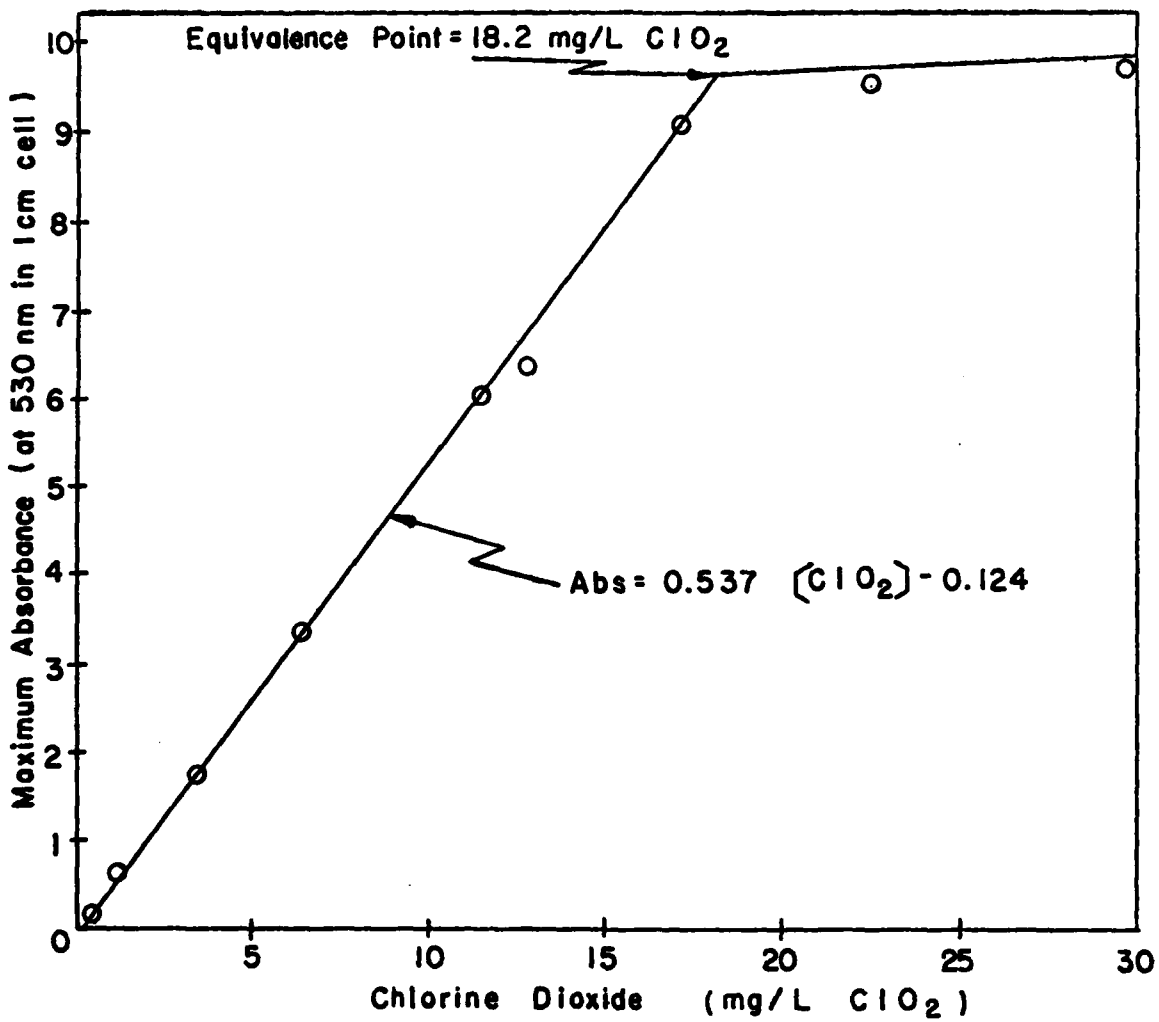


Figure 20. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Chlorine Dioxide and Syringaldazine in the Modified FACTS II Procedure Employing 3 mg of Potassium Iodide.

data are tabulated in Table B-1 of Appendix B. Additional data points are included for higher values of chlorine dioxide. These data were used to develop the linear regression for the line describing points after the equivalence point. The results of the linear regression are summarized in Table 6.

TABLE 6. EQUATIONS OF THE LINES OBTAINED FROM A LINEAR REGRESSION OF THE DATA FOR THE REACTION BETWEEN CHLORINE DIOXIDE AND SYRINGALDAZINE

Date	Equation
FACTS II Procedure	
2 December 1977	Abs = 0.354 [ClO_2] + 0.081
4 December 1977	Abs = 0.390 [ClO_2] + 0.064
11 December 1977	Abs = 0.405 [ClO_2] + 0.115
17 December 1977	Abs = 0.420 [ClO_2] + 0.066
4 March 78	Abs = 0.418 [ClO_2] - 0.007
Combined	Abs = 0.401 [ClO_2] + 0.003
Modified FACTS II Procedure	
4 March 1978	
~3 mg KI	Abs = 0.537 [ClO_2] - 0.124
~10-18 mg KI	Abs = 0.494 [ClO_2] - 0.046
~60 mg KI	Abs = 0.426 [ClO_2] - 0.004

The absorbance readings began to decrease at chlorine dioxide concentrations above 18 mg/L. At the high concentrations, there was no observable color at the 1-minute reaction point. This fading caused the tent-like plotted line shown in Figure 19. A possible explanation is that the chlorine dioxide may oxidize the colored product, forming a product that does not have an absorbance in the visible range. The rate constant for this reaction is probably smaller than the rate constant for the formation of the dye.

Figure 20 shows the results for the reaction of various concentrations of chlorine dioxide with the modified FACTS II procedure. This procedure did stabilize the color produced at the higher concentrations.

As with bromine and monobromamine, different amounts of KI were studied. The small amount, approximately 3 mg, produced the largest amount of color. The large amount, approximately 60 mg, seemed to inhibit color development. More than 5 minutes were required for maximum color development. The amount of color produced with 60 mg KI is similar to that produced in the FACTS II procedure. This is shown by the similar slopes of the two procedures: 0.401 with the FACTS II procedure and 0.426 with the modified FACTS II procedure. The raw data are tabulated in Table B-2 of Appendix B. Additional data were used to develop the linear regression for the line describing points in the plateau after the equivalence point.

In order to evaluate the daily reproducibility of both procedures, equations of the lines were determined for each day's data (Table 6). All data for all the days were used in determining the combined line.

In summary, it was found that aqueous solutions of chlorine dioxide, when reacted with the FACTS II procedure, obeyed Beer's Law through 18 mg/L, which is 2.7×10^{-4} M. When KI was added, the range through which Beer's Law was obeyed was 18.2 mg/L with 3 mg KI, which is 2.7×10^{-4} M ClO_2.

Fading. In order to develop a procedure for aqueous solutions of chlorine dioxide, it is necessary to minimize the fading of the colored product. Fading has occurred in previous studies that used the FACTS II procedure for determining chlorine. Therefore, experiments were undertaken to determine the extent of fading with the FACTS II and the modified FACTS II procedures for various concentrations of chlorine dioxide.

Fading was a problem in the FACTS II procedure at high concentrations. Figure 21 shows the amount of fading observed with the FACTS II procedure. The data are tabulated in Table B-4 of Appendix B. It was thought that the 0.1-cm cuvette was catalyzing the fading due to the large surface-to-volume ratio of the 0.1-cm cuvette. Any plating in this small cuvette would be more obvious than in a larger one. However, the cuvette was not the cause, because the fading was observed in the test tube. As soon as the FACTS II indicator was added, the characteristic red color was produced. At high concentrations, the color faded in the time required to invert the tube for mixing. The reaction solution remained in the test tube for 5 minutes (unless all color disappeared sooner) and fading was observed by eye. Therefore, the cuvette was not causing the fading at high concentrations. The chlorine dioxide, which is a strong oxidant, may have oxidized the colored product, causing the fading.

Fading was not a problem in the modified FACTS II procedure; the KI (3 mg) seemed to stabilize the reaction. Figure 22 shows the amount of fading observed with the modified FACTS II procedure. The data are tabulated in Table B-5 of Appendix B. There was less than 0.05 absorbance units of fading based on a 1.0-cm cuvette in the 5-minute reaction.

Lower Limit of Detection. No direct attempt was made to determine the lower limit of detection for chlorine dioxide. However, good results were obtained down to 0.39 mg/L chlorine dioxide with the FACTS II procedure.

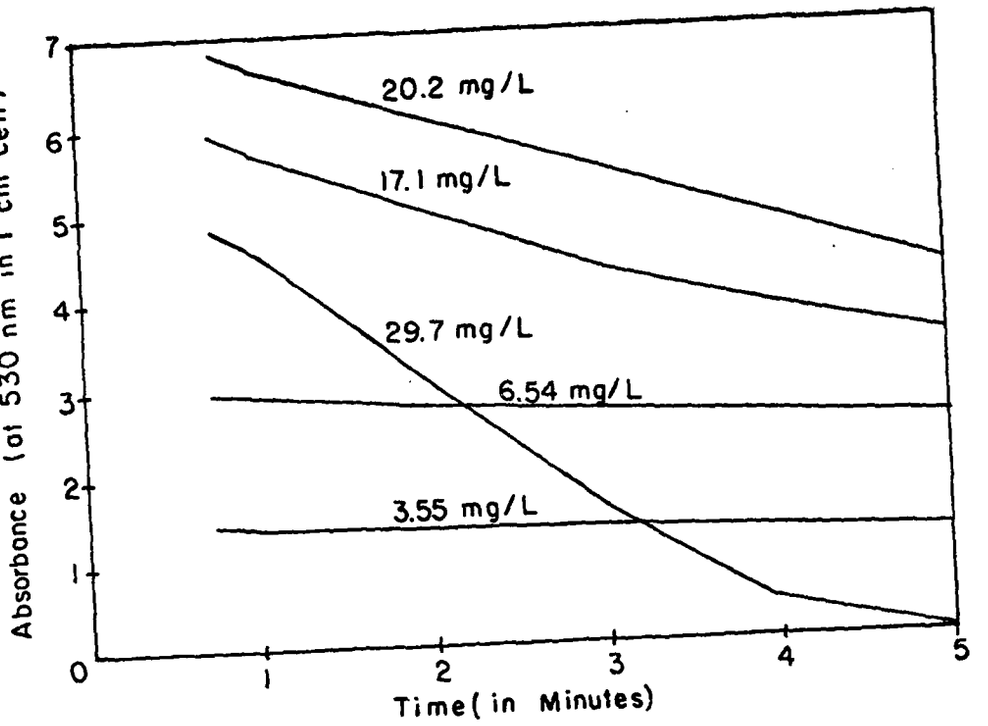


Figure 21. Color Fading in the FACTS II Procedure for Chlorine Dioxide.

An absorbance of 0.1 was observed in order to obtain the results for 0.39 mg/L. If 0.1 were accepted as the lowest readily observed (with the spectrophotometer) absorbance value, then the lower limit of detection for the modified FACTS II procedure would be 0.40 mg/L.

Stoichiometry. The Beer's Law plots (Figures 19 and 20) show the results of the spectrophotometric titrations of aqueous solutions of chlorine dioxide with the FACTS II and the modified FACTS II procedures. The stoichiometry of the reaction was determined by the mole ratio of chlorine dioxide to syringaldazine required for maximum color development. These mole ratios were determined from the ratios observed at the intercepts of the two straight lines in each curve. The intercept of the two lines is the equivalence point: the point at which the molar concentrations of chlorine dioxide and syringaldazine are equal.

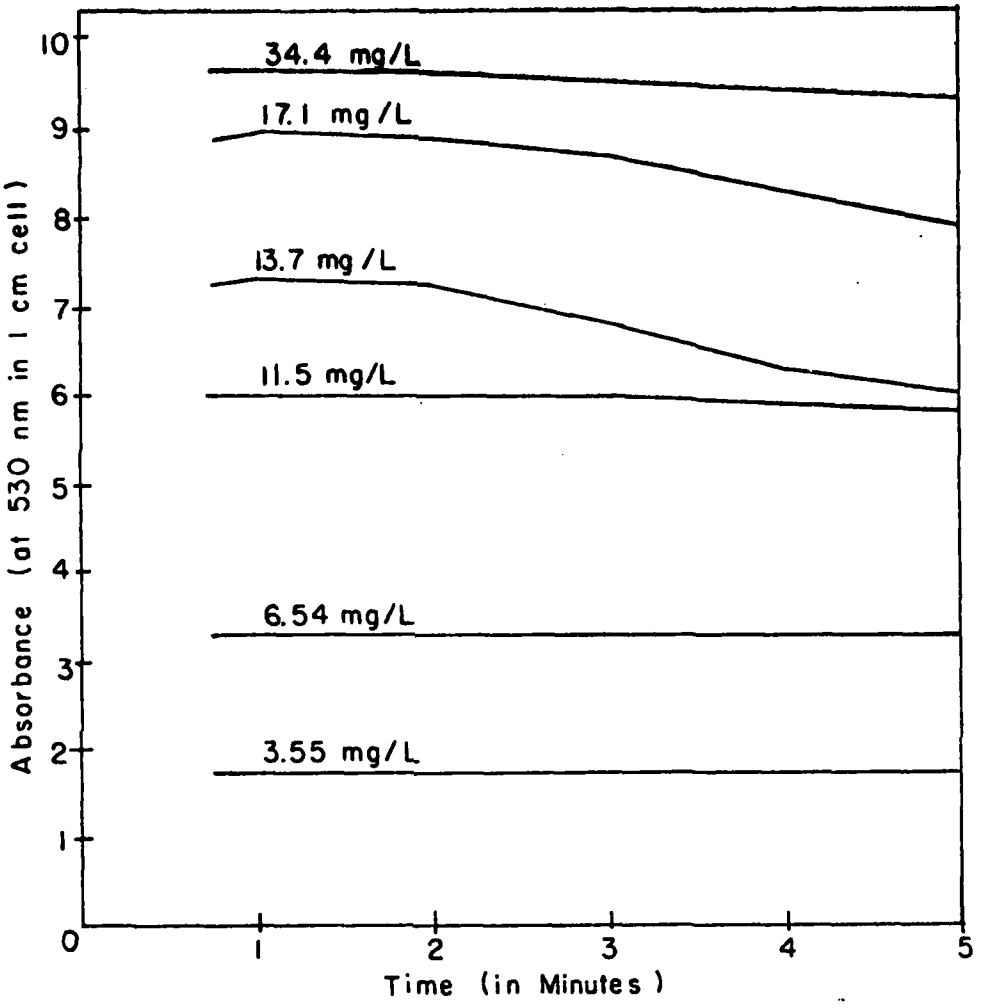


Figure 22. Color Fading in the Modified FACTS II Procedure for Chlorine Dioxide (3 mg potassium iodide used).

The equivalence point is determined by solving the simultaneous equations for ClO_2 concentration. The equations used were those that describe the Beer's Law portion of the plot and the plateau region.

The equivalence points and molar ratios are shown in Table 7. The mole ratio is determined the same way as shown in the sample calculation for bromine.

TABLE 7. EQUIVALENCE POINTS FOR THE REACTION BETWEEN CHLORINE DIOXIDE AND SYRINGALDAZINE

Date	Equivalence Point (mg/L)	Molar Ratio ClO_2:Syr
	FACTS II Procedure	
2 December 1977	19.3	2.18
4 December 1977	18.2	2.06
11 December 1977	17.7	2.00
17 December 1977	17.4	1.97
4 March 1978	17.6	1.99
Combined	18.0	2.04
	Modified FACTS II Procedure	
4 March 1978		
Amount KI		
~3 mg	18.2	2.06
~10-18 mg	18.9	2.14
~60 mg	19.0	2.15

The data in Table 7 indicate that the ratio of chlorine dioxide to syringaldazine in both the FACTS II and the modified FACTS II procedures is approximately 2 moles chlorine dioxide per mole of syringaldazine, as might be expected for this one-electron oxidant.

Iodine

Procedure Development. Initially, iodine was permitted to react with syringaldazine using the FACTS II procedure as developed for chlorine.[69] It was found that when aqueous solutions of iodine reacted directly with syringaldazine, a colored product was produced rapidly.

To facilitate comparison with earlier work,[76] the FACTS II procedure was modified to include the addition of 12 drops (1 mL) of CDFW to the iodine sample, which gave the same final volume, permitting direct comparison of absorbance. This variant procedure was as follows:

1. A 5-mL sample of the solution to be tested was pipetted into a 10-cm test tube.

2. Twelve drops (1 mL) of CDFW were added.

3. Two-tenths milliliter of FACTS II buffer was added.

4. The tube was capped and inverted several times to insure complete mixing.

5. Two milliliters of syringaldazine indicator solution (118 mg/L in 2-propanol) were added; the tube was capped and inverted twice to mix.

6. The absorbance of the solution at 530 nm was determined with a spectrophotometer. The readings were taken after 1 minute, with the use of a cuvette of appropriate path length. All readings were normalized to a 1-cm path length.

Experiments were conducted according to the above procedure to analyze aqueous solutions of iodine. The FACTS II procedures were compared to determine the effect of the additional milliliter of CDFW in the determination of aqueous solutions of iodine.

Concentration Range. Varying concentrations of iodine were prepared in CDFW. These solutions were used to determine the absorbance at 530 nm of the colored product using the FACTS II procedure and the FACTS II procedure with dilution. The results are shown graphically in Figures 23 and 24.

Figure 23 shows the results of the reaction of various concentrations of iodine with the FACTS II procedure. The absorbance for each sample is the observation after 1 minute of reaction of iodine with syringaldazine, in accordance with the FACTS II procedure. The raw data are tabulated in Appendix C, Table C-1. Additional data points are included for higher values of iodine. These data were used to develop the linear regression for the line describing points in the plateau after the equivalence point.

Figure 24 shows the results for the reaction of various concentrations of iodine with the FACTS II procedure with dilution. The absorbance for each sample is the observation after a 1-minute reaction of iodine with syringaldazine, in accordance with the FACTS II procedure with dilution. The raw data are tabulated in Table C-2 of Appendix C. Additional data points are included for higher values of iodine. All the data were used to develop the linear regression for the line describing points in the plateau after the equivalence point.

In order to evaluate the daily reproducibility of both procedures, equations of the lines were determined for each day's data (Table 8). All data for all the days were used in determining the combined line.

In summary, it was found that aqueous solutions of iodine, when reacted with FACTS II, obeyed Beer's Law through 28.5 mg/L, which is 1.1×10^{-4} M. When the procedure was modified by the addition of water, the range through which Beer's Law was obeyed was 31.8 mg/L, which is 1.25×10^{-4} M.

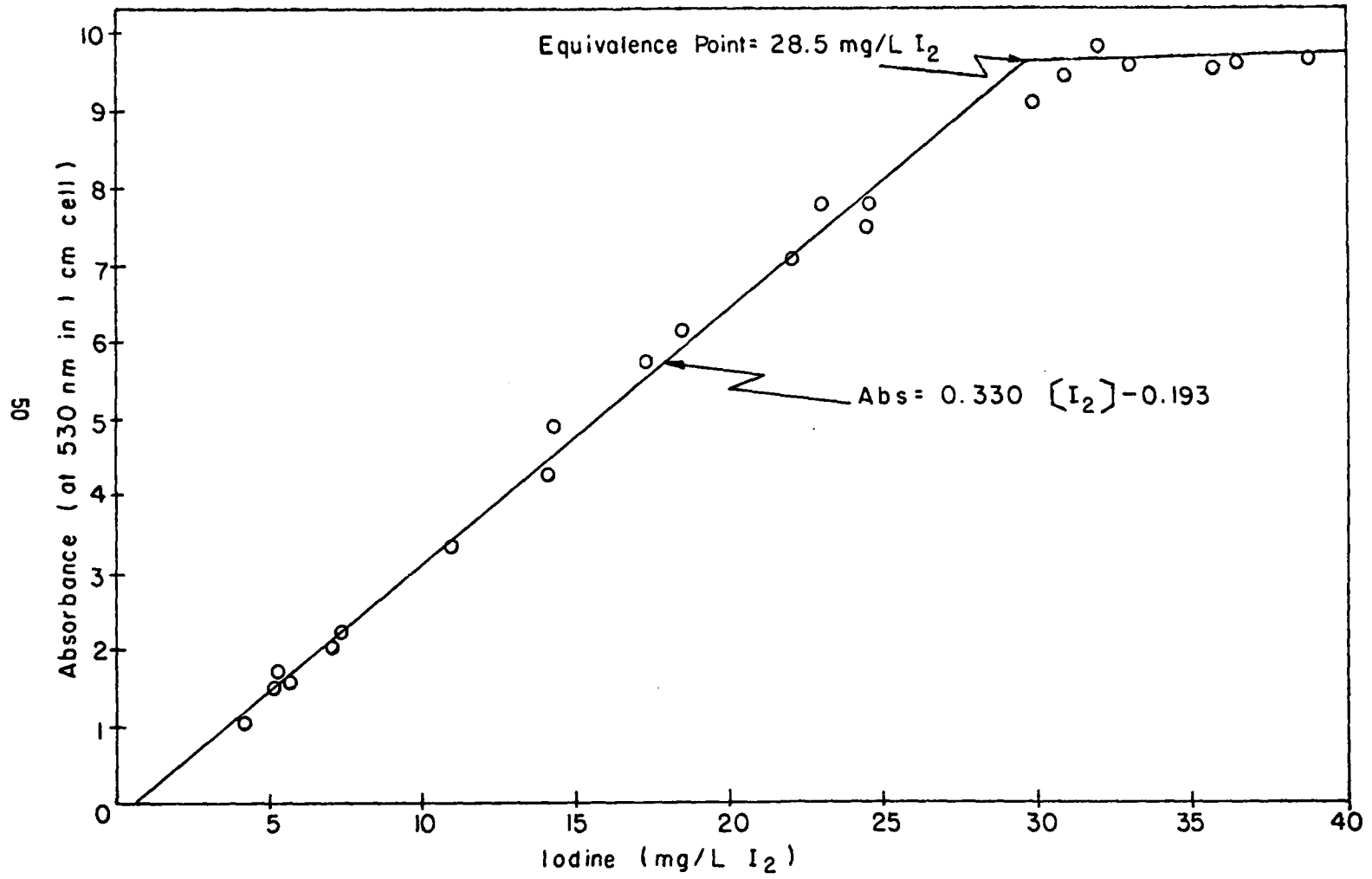


Figure 23. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Iodine and Syringaldazine in the FACTS II Procedure.

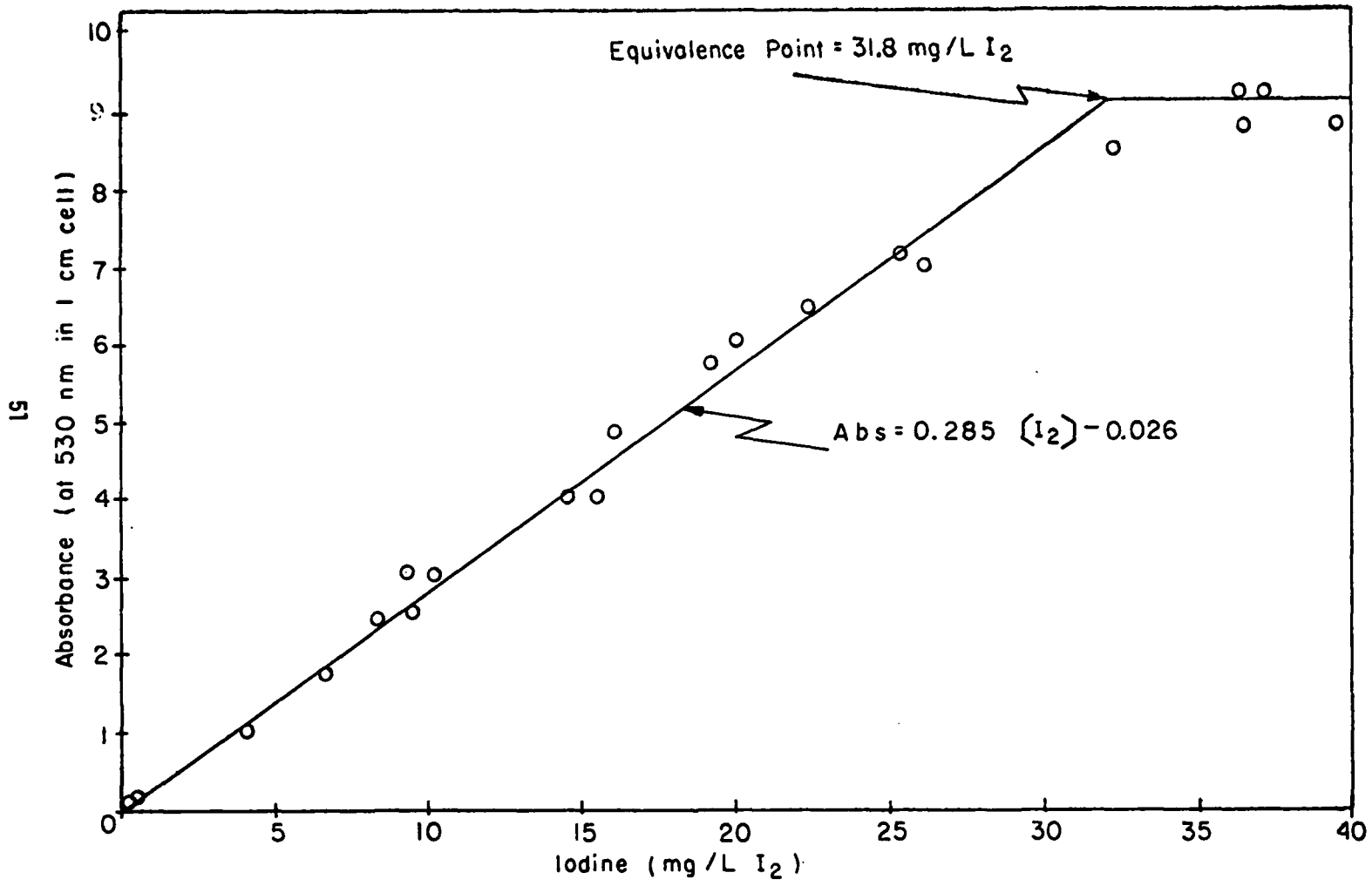


Figure 24. Beer's Law Plot of the Absorbances Resulting from Reaction Between Various Concentrations of Iodine and Syringaldazine in the FACTS II Procedure with Dilution.

TABLE 8. EQUATIONS OF THE LINES OBTAINED FOR A LINEAR REGRESSION OF THE DATA FOR THE REACTION BETWEEN IODINE AND SYRINGALDAZINE

Date	Equation
FACTS II Procedure	
24 October 1977	Abs = 0.347 $[I_2]$ - 0.297
25 October 1977	Abs = 0.312 $[I_2]$ - 0.094
26 October 1977	Abs = 0.310 $[I_2]$ + 0.003
Combined	Abs = 0.330 $[I_2]$ - 0.193
FACTS II Procedure with Dilution	
8 August 1977	Abs = 0.305 $[I_2]$ - 0.083
9 August 1977	Abs = 0.270 $[I_2]$ + 0.007
20 August 1977	Abs = 0.271 $[I_2]$ + 0.113
Combined	Abs = 0.265 $[I_2]$ - 0.026

Fading. In order to develop a procedure for aqueous solutions of iodine, it is necessary to minimize the fading of the colored product. Fading has occurred in previous studies that used the FACTS II procedure for determining chlorine. Therefore, experiments were undertaken to determine the extent of fading with FACTS II procedure and FACTS II procedure with dilution for various concentrations of iodine.

Fading was a problem in the reaction of iodine with both the FACTS II and the FACTS II variant with dilution procedure (Figs. 25 and 26). Data are tabulated in Tables C-5 and C-6 of Appendix C, respectively.

By observation, a probable cause of the fading was the 0.1-cm cuvette since the surface-to-volume ratio in the 0.1-cm cuvette is larger than in the 1.0-cm cuvette. This was tested by allowing the reaction mixture to remain in a test tube for the 5-minute reaction. The absorbance was then observed in the 0.1-cm cuvette. Only slight fading had occurred compared to the fading that occurred in the 0.1-cm cuvette. Therefore, this fading could be an interference when the smaller cuvette was used for determining higher concentrations of iodine.

Lower Limit of Detection. No direct attempt was made to determine the lower limit of detection for iodine. However, low concentration samples were tested and good results were obtained down to 0.12 mg/L iodine.

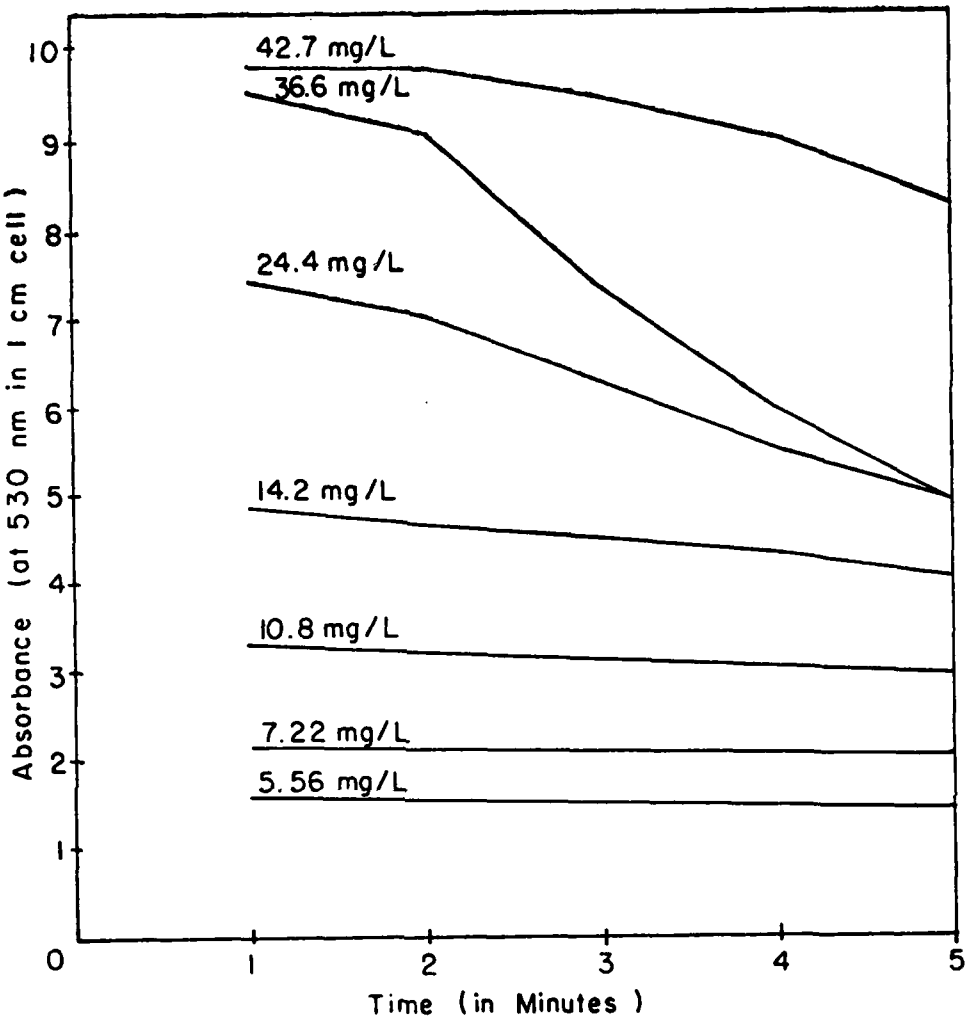


Figure 25. Color Fading in the FACTS II Procedure for Iodine.

Stoichiometry. The Beer's Law plots (Figures 23 and 24) show the results of the spectrophotometric titrations of aqueous solutions of iodine with the FACTS II and the FACTS II with dilution procedures. The stoichiometry of the reaction was determined by the mole ratio of iodine to syringaldazine required for maximum color development. These mole ratios were determined from the ratios observed at the intercepts of the two straight lines in each curve. The intercept of the two lines is the equivalence point: the point at which the molar concentrations of the oxidant and syringaldazine are equal. The equivalence point is determined by solving the simultaneous equations for I_2 concentration. The equations used were those that describe the Beer's Law portion of the plot and the plateau region.

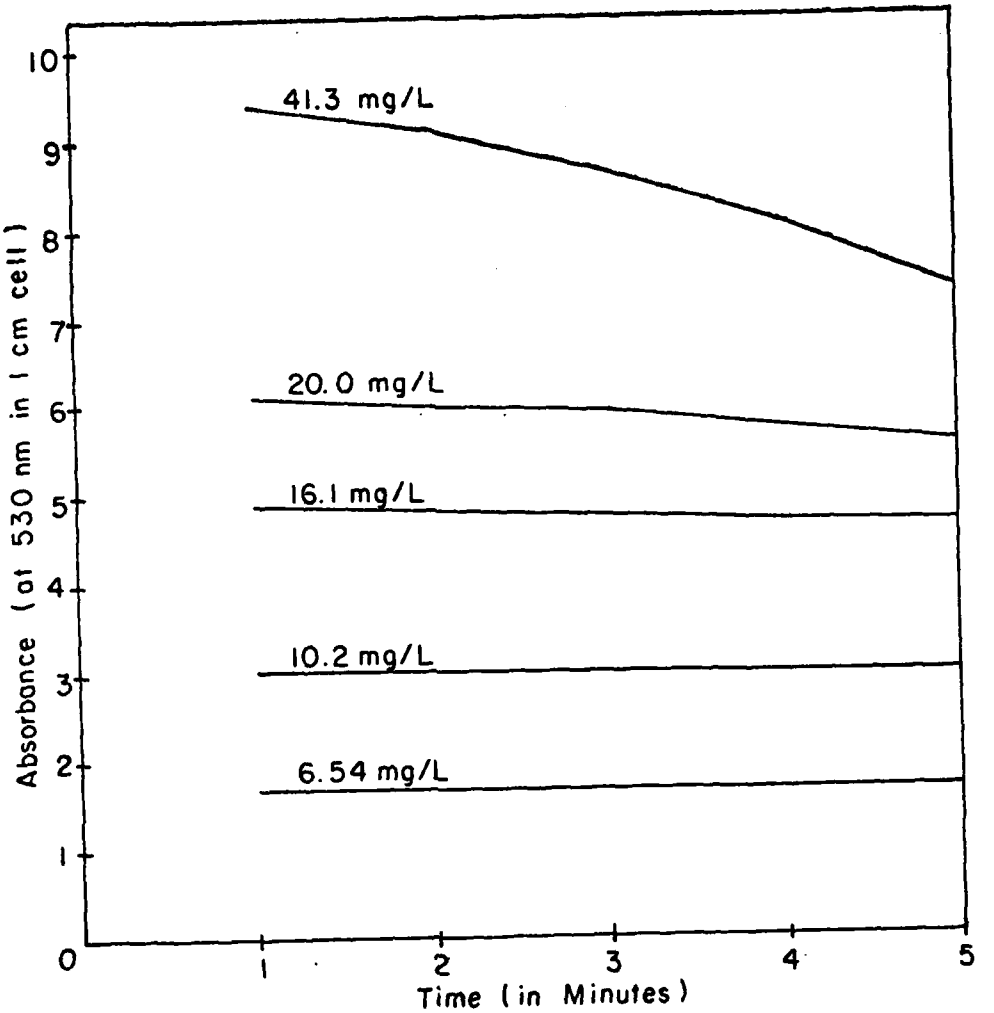


Figure 26. Color Fading in the FACTS II Procedure with Dilution for Iodine.

The equivalence points and molar ratios are shown in Table 9. The mole ratio was determined by the same procedure as that given for bromine.

The data in Table 9 indicate that the ratio of iodine to syringaldazine in both the FACTS II procedure and the FACTS II procedure with dilution is a little less than 1 mole of I_2 per mole of syringaldazine.

Organically Polluted Water. No studies were performed on organically polluted water with iodine because there is no reason to believe that iodine would react with ammonia to form iodamines.

TABLE 9. EQUIVALENCE POINTS FOR THE REACTION BETWEEN IODINE AND SYRINGALDAZINE

Date	Equivalence Point (mg/L)	Molar Ratio I_2:Syr
	FACTS II Procedure	
24 October 1977	28.9	0.87
25 October 1977	31.3	0.94
26 October 1977	30.7	0.92
Combined	28.5	0.86
	FACTS II Procedure with Dilution	
8 August 1977	31.0	0.93
9 August 1977	33.9	1.02
20 August 1977	32.1	0.97
Combined	31.8	0.96

CONCLUSIONS

The FACTS II procedure has been modified to determine total available bromine, chlorine dioxide, and iodine in aqueous solutions. The modified FACTS II procedure for bromine was tested using organically polluted water to which bromine had been added. The modified FACTS II procedure, compared to amperometric titration, gave acceptable results.

The modified FACTS II procedures in unpolluted water obey Beer's Law through the range of 0 to 26 mg/L bromine, 1.6×10^{-4} M; through the range of 0 to 18 mg/L monobromamine, 1.8×10^{-4} M; and through the range of 0 to 18 mg/L chlorine dioxide, 2.7×10^{-4} M. The FACTS II procedure with dilution obeyed Beer's Law through the range of 0 to 31 mg/L iodine, 1.2×10^{-4} M. The theoretical lower limit of detection was shown to be 0.4 mg/L for bromine (as Br_2), and 1.1 mg/L for monobromamine (as NH_2Br). The actual lower limit of detection was shown to be 0.39 mg/L for chlorine dioxide (as ClO_2) and 0.12 mg/L for iodine (as I_2).

The maximum color was found to develop within 1 minute with the modified FACTS II procedure for all oxidants. In most samples, the color was stable for a 5-minute reaction period. In some cases, the higher concentrations of oxidant did show fading during the 5 minutes, a fading comparable to that of the FACTS II procedure.

Although all three amounts of added KI (3, 10 to 18, or 60 mg) were satisfactory with monobromamine in the modified FACTS II procedure, best results were obtained with the least amount (3 mg) for chlorine dioxide determination and with a medium amount (10 to 18 mg) for bromine determination.

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APPENDIX A

Experimental Data for the Development of the FACTS Procedure for the Determination of Bromine and Monobromamine in Aqueous Solution

TABLE A-1. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF BROMINE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE

Date	Conc. mg/L Br_2	Absorbance Min (average)	Absorbance Maximum
	~10 to 18 mg KI		
19 February 1978	24.9	6.29	6.47
	21.9	6.34	6.47
	17.0	4.67	4.87
	15.3	3.84	3.87
	10.1	2.50	2.51
	5.44	1.63	1.69
	1.48	0.326	0.327
	~3 mg KI		
25 February 1978	29.9	4.78	4.79
	24.3	3.95	3.95
	18.4	3.22	3.22
	11.3	2.31	2.31
	5.10	1.15	1.15
	~10 to 18 mg KI[a]		
	29.9	7.20	7.21
	24.3	6.71	7.10
	18.4	5.10	5.13
	11.3	2.35	2.36
	5.10	1.59	1.66
	~60 mg KI		
	29.9	7.95	8.66
	24.3	6.01	7.44
	18.4	4.63	5.16
	11.3	3.26	3.33
	5.10	1.76	2.07

All absorbance readings are corrected to 1.0-cm path length.

a. These data (~ 10 to 18 mg KI) were used in conjunction with 19 February 1978 data to determine equations for the lines.

TABLE A-2. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF MONOBROMAMINE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE

Date	Conc. mg/L NH_2Br	Absorbance T Min	Absorbance Maximum
	~3 mg KI		
14 February 1978	33.9	9.07	9.12
	15.7	9.56	9.57
	7.17	3.62	3.64
	5.29	2.34	2.36
26 February 1978	45.5	9.09	9.14
	17.7	9.44	9.48
	12.9	7.43	7.48
	6.85	3.11	3.11
	5.69	2.25	2.27
18 March 1978	49.9	9.21	9.25
	23.7	9.59	9.64
	11.5	6.72	6.77
	8.15	4.70	4.73
	6.74	3.22	3.25
	3.53	1.64	1.65
	~10 to 18 mg KI		
26 February 1978	45.5	8.76	8.80
	17.7	9.43	9.45
	12.9	7.49	7.53
	6.85	3.14	3.15
	5.69	2.22	2.26
	~60 mg KI		
26 February 1978	45.5	8.48	8.61
	17.7	8.50	8.88
	12.9	7.26	7.26
	6.85	3.16	3.16
	5.69	2.28	2.29
18 March 1978	49.9	8.02	8.12
	23.7	9.32	9.39
	11.5	6.84	6.85
	8.15	4.80	4.82
	6.74	3.36	3.40
	3.53	1.64	1.65

All absorbance readings are corrected to 1.0-cm path length.

TABLE A-3. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF BROMINE IN AQUEOUS SOLUTION USING THE FACTS II PROCEDURE

Date	Conc. mg/L Br_2	Absorbance 1 Min	Average
7 September 1977	43.4	6.27, 6.35, 6.37	6.33
	35.9	6.11, 6.39, 6.14, 6.19, 6.20, 6.35	6.23
	28.6	5.81, 5.90, 5.80, 5.84	5.84
	22.4	5.10, 5.13, 4.92, 4.80, 4.98, 4.99	4.99
	17.8	4.73, 4.80, 4.67, 4.79	4.75
	12.5	3.77, 3.65, 3.78, 3.64	3.71
	8.82	2.60, 2.68, 2.62	2.63
9 September 1977	16.4	4.60, 4.55, 4.68, 4.57, 4.64, 4.61	4.61
	13.0	3.76, 3.77	3.77
	10.1	2.92, 2.96, 2.93	2.93
	6.99	2.37, 2.36	2.37
	4.52	1.43, 1.49, 1.43	1.45
	2.62	0.645, 0.630	0.640
19 February 1978	24.9	5.98, 5.66, 6.08, 5.79	5.88
	21.9	5.30, 5.42, 5.23	5.31
	17.0	4.58, 4.46, 4.40	4.48
	15.3	4.16, 4.07, 4.20	4.14
	10.1	2.83, 2.90, 2.80	2.84
	5.44	1.65, 1.67	1.66
	1.48	0.163, 0.128, 0.155	0.149
25 February 1978	35.1	6.96, 7.28, 7.02, 6.95	7.05
	29.9	6.45, 6.47, 6.56	6.49
	24.3	5.93, 5.70, 5.80	5.81
	18.4	5.01, 4.95, 4.75, 4.72	4.86
	16.7	4.47, 4.41, 4.51	4.46
	11.3	3.39, 3.37, 3.32	3.36
	5.10	1.55, 1.60, 1.55	1.57

All absorbance readings are corrected to 1.0-cm path length.

TABLE A-4. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF MONOBROMAMINE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE

Date	Conc. mg/L NH_2Br	Absorbance 1 Min	Absorbance 5 Min	Absorbance Maximum
29 January 1978	29.0	6.50	7.55	8.08
	26.0	--[a]	8.25	8.25
	13.6	--	5.47	5.51
	9.47	--	3.87	3.95
	4.51	--	1.46	1.48
	2.91	--	0.436	0.438
4 February 1978	28.3	--	10.7	10.7[b]
	23.4	--	9.84	9.91[b]
	20.7	--	9.12	9.25[b]
	4.30	--	1.47	1.48[b]
	4.27	--	1.36	1.38[b]
	2.83	--	0.536	0.536
	2.00	--	0.168	0.168
14 February 1978[c]	33.9	8.22	8.15	8.74
	15.7	5.28	6.71	6.83
	7.17	1.87	2.95	3.00
	5.29	1.61	1.85	1.96
26 February 1978[c]	45.5	8.40	7.46	8.40[b]
	17.7	5.99	7.39	7.46[b]
	12.9	5.30	5.66	6.31[b]
	6.85	2.23	2.64	2.80[b]
	5.69	1.65	1.79	2.01[b]
18 March 1978[c]	49.9	8.13	7.77	8.37
	23.7	7.16	7.86	8.39
	11.5	4.83	5.17	5.70
	8.15	3.10	3.96	4.05
	6.74	1.99	2.01	2.27
	3.53	1.11	1.21	1.32

All absorbance readings are corrected to 1.0-cm path length.

a. Not observed.

b. Maximum absorbance was beyond 5-minute reaction time.

c. Observed on the ACTA CV; all others on this page were done on the Spec 700.

TABLE A-5. FADING OF THE COLOR PRODUCED AT 530 nm BY VARIOUS CONCENTRATIONS OF BROMINE ON AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE

Date	Conc. mg/L Br_2	Absorbance 1 Min	Absorbance 5 Min	Δ	% Decrease
7 September 1977	43.4	6.33	5.40	0.93	14.7
	35.9	6.23	5.29	0.94	15.1
	28.6	5.84	5.10	0.74	12.7
	22.4	4.99	4.34	0.65	13.0
	17.8	4.75	4.39	0.36	7.6
	12.5	3.71	3.51	0.20	5.4
	8.82	2.63	2.48	0.15	5.7
9 September 1977	16.4	4.61	4.29	0.32	6.9
	13.0	3.77	3.50	0.27	7.2
	10.1	2.93	2.75	0.18	6.1
	6.99	2.37	2.21	0.16	6.8
	4.52	1.45	1.39	0.06	4.1
	2.62	0.640	0.580	0.06	9.4
19 February 1978	24.9	5.88	5.20	0.68	11.6
	21.9	5.31	4.88	0.43	8.1
	17.0	4.48	3.97	0.51	11.4
	15.3	4.14	3.78	0.36	8.7
	10.1	2.84	2.60	0.24	8.5
	5.44	1.66	1.62	0.04	2.4
	1.48	0.149	0.149	0.0	0.0
25 February 1978	35.1	7.05	6.24	0.81	11.5
	29.9	6.49	5.51	0.98	15.1
	24.3	5.81	5.06	0.75	12.9
	18.4	4.86	4.20	0.66	13.6
	16.7	4.46	4.07	0.39	8.7
	11.3	3.36	3.04	0.32	9.5
	5.10	1.57	1.55	0.02	1.3

All absorbance readings are corrected to 1.0-cm path length.

TABLE A-6. FADING OF THE COLOR PRODUCED AT 530 nm BY VARIOUS CONCENTRATIONS OF BROMINE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE

Date	Conc. mg/L Br_2	Absorbance 1 Min	Absorbance 5 Min	Δ	% Decrease
		~10 to 18 mg KI			
19 February 1978	24.9	6.29	6.29[a]	0.0	0.0
	21.9	6.34	6.21	0.13	2.1
	17.0	4.67	4.56	0.11	2.4
	15.3	3.84	3.67	0.17	4.4
	10.1	2.50	2.42	0.08	3.2
	5.44	1.63	1.69[b]	+0.06	+3.7
		~3 mg KI			
25 February 1978	29.9	4.78	4.31	0.47	9.8
	24.3	3.95	3.64	0.31	7.8
	18.4	3.22	2.97	0.25	7.8
	11.3	2.31	2.14	0.17	7.4
	5.10	1.15	1.15	0.0	0.0
		~10 to 18 mg KI			
	29.9	7.20	6.57	0.63	8.8
	24.3	6.71	6.37	0.34	5.1
	18.4	5.10	4.84	0.26	5.1
	11.3	2.35	2.14	0.21	8.9
	5.10	1.59	1.61	+0.02	+2.5
		~60 mg KI			
	29.9	7.95	8.23	+0.28	+3.5
	24.3	6.01	7.44	+1.43	+23.8
	18.4	4.63	4.92	+0.29	+6.3
	11.3	3.26	3.35	+0.09	+2.7
	5.10	1.76	2.06	+0.30	+17.0

All absorbance readings are corrected to 1.0-cm path length.
a. Not stable; increased then decreased during 5 minutes.
b. Maximum was between 4 and 5 minutes.

TABLE A-7. COLOR DEVELOPMENT OF VARIOUS CONCENTRATIONS OF MONOBROMAMINE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE

Date	Conc. mg/L NH_2Br	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
29 January 1978	29.0	--[a]	--[a]	0.790	0.805	0.760	0.725
		--	--	0.795	0.812	0.787	0.745
		--	--	0.775	0.805	0.807	0.795
	26.0	--	6.50	7.75	8.12	8.25	8.25
	13.6	--	--	--	5.32	5.57	5.62
		--	--	--	5.30	5.55	5.62
		--	--	--	5.27	5.30	5.20
	9.47	--	--	--	3.85	4.02	4.10[b]
		--	--	--	3.80	4.00	4.07[b]
		--	--	--	3.55	3.60	3.67[b]
	4.51	--	--	--	1.39	1.44	1.45
		--	--	--	1.45	1.48	1.48
		--	--	--	1.47	1.50	1.49
	2.91	--	--	--	0.445	0.445	0.440
		--	--	--	0.445	0.447	0.447
		--	--	--	0.420	0.422	0.420
4 February 1978	28.3	--	--	--	10.4	10.6	10.7
		--	--	--	--	10.7	10.8
		--	--	--	10.3	10.6	10.7
	23.4	--	--	--	9.17	9.65	9.90[b]
		--	--	--	9.25	9.72	9.87[b]
		--	--	--	9.15	9.57	9.87[b]
	20.7	--	--	--	8.55	9.00	9.32[b]
		--	--	--	8.57	8.97	9.12[b]
		--	--	--	8.60	9.10	9.32[b]
	4.30	--	--	--	1.33	1.43	1.49[b]
		--	--	--	1.30	1.42	1.47[b]
		--	--	--	1.32	1.42	1.47[b]
		--	--	--	1.34	1.43	1.47[b]
	4.27	--	--	--	1.37	1.41	1.43[b]
		--	--	--	1.20	1.30	1.37[b]
		--	--	--	1.18	1.28	1.35[b]
		--	--	--	1.20	1.29	1.36[b]

TABLE A-7 (Continued)

Date	Conc. mg/L NH_2Br	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
	2.83	--	--	--	0.492	0.522	0.535
		--	--	--	0.487	0.520	0.532[b]
		--	--	--	0.487	0.520	0.540[b]
	2.00	--	--	--	0.167	0.167	0.167
		--	--	--	0.167	0.170	0.170
		--	--	--	0.165	0.167	0.167
14 February 1978	33.9	--	8.65	8.96	8.83	8.55	8.35
		--	8.04	8.69	8.59	8.33	7.92
		--	7.98	8.57	8.49	8.33	8.17
	15.7	4.92	5.84	6.78	6.85	6.78	6.71
		5.19	5.71	6.92	7.20	7.19	7.10
		3.89	5.15	5.72	6.23	6.44	6.32
	7.17	--	1.84	2.55	2.84	2.93	2.95
		1.64	1.87	2.59	2.86	2.93	2.88
		1.70	1.89	2.65	3.12	3.13	3.02
	5.29	--	1.73	2.02	1.96	1.92	1.88
		2.20	2.19	2.15	2.11	2.06	2.01
		1.30	1.52	1.87	1.93	1.89	1.84
		1.34	1.55	1.88	1.92	1.86	1.80
		--	1.07	1.51	1.74	1.72	1.79
26 February 1978	45.4	8.15	8.32	8.14	7.93	7.70	7.50
		8.22	8.47	8.34	7.98	7.66	7.42
	17.7	5.35	6.03	7.39	7.60	7.67	7.54
		5.02	5.94	--	--	--	7.24
	12.9	4.62	5.24	6.40	6.46	6.12	5.68
		5.17	5.73	6.43	6.39	6.17	5.91
		4.27	4.94	5.98	6.05	5.72	5.39
	6.85	2.25	2.77	2.94	2.84	2.81	2.75
		1.79	2.07	2.64	2.79	2.70	2.59
		1.67	1.97	--	2.66	2.63	2.60
	5.69	2.12	2.17	2.11	2.04	1.92	1.82
		1.23	1.42	1.83	1.93	1.89	1.78
		1.13	1.37	--	--	--	1.78

TABLE A-7 (Continued)

Date	Conc. mg/L NH_2Br	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
18 March 1978	49.9	7.80	8.38[c]	8.30	8.18	7.97	7.80
		7.71	8.37[c]	8.30	8.13	7.92	7.70
		7.47	8.00	8.37	8.18	7.90	7.80
	23.7	6.68	7.45	8.55	8.61	8.32	7.91
		6.41	7.17	8.22	8.33	8.03	7.66
		6.08	6.86	8.06	8.22	8.00	8.00
	11.5	6.17	6.37	6.25	6.00	5.77	5.48
		4.84	6.37[c]	6.23	5.87	5.64	5.43
		3.19	3.76	--	5.21	5.17	4.92
		3.08	3.65	4.77	--	--	4.85
	8.15	2.00	2.34	3.23	3.56	3.69	3.67
		2.02	2.44	3.32	3.69	3.82	3.81
		3.82	4.22	4.52	--	--	4.42
		2.95	3.41	4.11	4.18	4.12	3.96
	6.74	--	2.42[c]	2.39	2.24	2.13	1.97
		1.91	2.13	2.40	2.30	2.26	2.14
		1.31	1.52	1.91	1.99	1.97	1.91
	3.53	1.27	1.41[c]	1.39	1.35	1.30	1.23
		0.610	0.780	1.10	1.23	1.24	1.24
		1.04	1.17	1.30	1.26	1.20	1.15

a. Not observed.
b. Maximum observation was at 5.5 minutes.
c. Maximum observation was at 1.5 minutes.

TABLE A-8. COLOR DEVELOPMENT OF VARIOUS CONCENTRATIONS OF MONOBROMAMINE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE WITH 3 mg KI

Date	Conc. mg/L NH_2Br	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
14 February 1978	33.9	--[a]	8.49	8.30	8.19	8.06	7.79
		--	9.22	9.13	8.85	--	8.70
		9.40	9.36	9.23	9.12	9.01	8.83
		9.39	9.35	9.08	8.97	8.86	8.58
	15.7	--	9.55	9.43	9.26	8.99	8.30
		9.55	9.55	9.42	9.08	8.70	8.25
		9.61	9.59	9.24	8.88	8.52	8.10
	7.17	3.66	3.65	3.57	3.49	3.39	3.30
		3.66	3.64	3.53	3.44	3.37	3.33
		3.61	3.59	3.51	3.38	3.30	3.21
	5.29	2.38	2.36	2.31	2.28	2.23	2.17
		2.41	2.38	2.29	2.18	2.07	1.95
		2.30	2.29	2.25	2.19	2.13	2.07
		2.32	2.34	2.26	2.20	2.15	2.08
26 February 1978	45.5	9.32	9.28	9.10	8.91	8.77	8.67
		8.95	8.90	8.74	8.62	8.47	8.37
	17.7	9.49	9.47	9.23	8.97	8.14	7.66
		9.46	9.41	--	--	--	8.42
	12.9	7.50	7.45	7.17	6.89	6.55	6.38
		7.45	7.40	7.06	6.77	6.24	5.82
	6.85	3.15	3.15	3.08	3.03	2.99	2.88
		3.09	3.07	--	--	--	2.71
	5.69	2.28	2.26	2.20	2.09	1.98	1.89
		2.26	2.23	2.16	2.01	1.88	1.80
18 March 1978	49.9	9.53	9.50	9.30	9.17	8.91	8.70
		8.95	8.90[b]	8.60	8.43	8.25	8.00
		9.39	9.44[b]	9.40	9.30	9.25	9.06
		9.07	9.03	8.73	8.63	8.40	8.09
	23.7	9.62	9.57	--	8.86	8.45	7.92
		9.60	9.55	9.29	8.92	8.56	8.13
		9.71	9.65	--	--	--	8.50

TABLE A-8 (Continued)

Date	Conc. mg/L NH_2Br	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
	11.5	6.78	6.74	6.58	6.40	6.18	5.95
		6.87	6.83	6.63	6.39	6.15	5.88
		6.65	6.60	--	--	--	5.57
	8.15	4.76	4.74	4.69	4.60	4.48	4.39
		4.72	4.70	4.55	4.43	4.30	4.16
		4.71	4.68	4.56	4.43	4.27	4.08
	6.74	3.18	3.20	3.12	3.00	2.86	2.70
		3.30	3.26	3.10	2.88	2.70	2.59
		3.26	3.21	3.07	2.95	2.77	2.56
	3.53	1.65	1.64	1.60	1.54	1.46	1.40
		1.64	1.63	1.63	1.63	1.60	1.51
		1.65	1.65	1.66	1.64	1.57	1.45

a. Not observed.
b. Maximum observation was at 1.5 minutes.

TABLE A-9. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS RESIDUAL BROMINE CONCENTRATIONS IN AN ORGANICALLY POLLUTED WATER

Date	Bromine Added (mg/L Br_2)	Total Bromine (mg/L Br_2)	Absorbance	
			FACTS II	FACTS II Mod[a]
16 February 1978[b]	114.0	36.9	7.39	9.35
	91.2	26.8	4.66	7.53
17 February 1978[b]	45.6	10.8	0.65	3.35
	34.2	3.82	0.118[c]	1.467
	22.8	2.39	0.091	0.857
	11.4	1.16	0.039	0.288
10 March 1978[d]	45.6	23.0	5.41	4.45
	33.7	18.4	3.21	3.40
	27.0	11.3	1.70	2.62
	22.8	6.56	0.553	1.98
	20.3	7.00	1.12	1.93
	18.1	3.67	0.551	1.19
	17.0	4.08	0.393	1.37
	11.4	1.52	0.176	0.360
	9.08	0.653	0.039	0.149

All absorbance readings are corrected to 1.0-cm path length.
Absorbances are average of three points.

a. Test with addition of 3 mg KI.
b. As treated, the water contained about 5 mg/L of ammonia nitrogen.
c. Did not reach a maximum within 10 minutes.
d. As treated, the water contained about 6.5 mg/L of ammonia nitrogen.

APPENDIX B

Experimental Data for the Development of the FACTS Procedure for the Determination of Chlorine Dioxide in Aqueous Solution

TABLE B-1. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF CHLORINE DIOXIDE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE

Date	Conc. mg/L ClO_2	Absorbance 1 Min	Average
2 December 1977	13.1[a]	4.52, 4.55, 4.45	4.50
	13.0	4.65, 4.69, 4.80, 4.72	4.71
	11.2	4.02, 4.02, 3.90	3.98
	9.36[a]	3.49, 3.31, 3.37	3.39
	7.28[a]	2.15, 2.15	2.15
	5.04	1.94, 1.92	1.93
	2.83	1.12, 1.13, 1.10, 1.09, 1.09	1.11
	1.84	0.677, 0.680, 0.669, 0.670	0.674
4 December 1977	36.9	2.25, 2.49, 2.30, 2.49	2.38
	20.2[a]	6.45, 6.62, 6.62, 6.35, 6.50, 6.77	6.55
	19.1[a]	6.30, 6.57, 6.50, 6.45	6.46
	17.5[a,b]	6.45, 6.25, 6.30, 6.32	6.33
	14.1[a,b]	5.32, 5.37, 5.12, 5.27, 5.07, 5.07	5.20
	14.0[a,b]	5.17, 5.12, 5.20, 5.07	5.14
	12.6	4.95, 4.99, 4.85	4.93
	9.72	3.77, 3.82, 3.92, 3.82	3.83
	8.03	3.38, 3.27, 3.38	3.34
	6.12	2.42, 2.45, 2.42	2.43
	3.83	1.57, 1.56, 1.56	1.56
	2.22	0.915, 0.932, 0.907, 0.885, 0.885	0.905
	1.66	0.702, 0.701, 0.692, 0.692	0.697
11 December 1977	23.4[a,b]	5.50, 5.65, 5.72, 5.92, 6.02	5.76
	20.8[b]	6.50, 6.45, 6.47	6.47
	21.3[a,b]	6.37, 6.30, 6.35	6.34
	17.9[a,b]	6.80, 6.75, 6.69, 6.70	6.74
	16.7[a,b]	6.22, 6.47, 6.45, 6.20, 6.37, 6.15, 6.40, 6.30	6.32
	14.0[b]	5.77, 5.70, 5.70	5.72
	8.64[b]	3.82, 3.67, 3.67	3.72
	6.21[b]	2.77, 2.75, 2.72	2.75
	4.13[b]	1.64, 1.67, 1.66, 1.65, 1.62, 1.62	1.64

TABLE B-1 (Continued)

Date	Conc. mg/L ClO_2	Absorbance 1 Min	Absorbance Average
17 December 1977	23.4[b]	6.03, 6.19, 6.16, 6.35, 6.30	6.21
	19.1[b]	6.70, 6.82, 7.20, 7.08	6.95
	16.3[a,b]	6.70, 6.57, 6.47, 6.42	6.54
	14.0[b]	6.05, 5.82, 5.85, 5.82	5.89
	13.7[b]	5.72, 5.70, 5.67	5.70
	10.1[b]	4.40, 4.35, 4.42	4.39
	7.48[b]	3.45, 3.32, 3.39	3.39
	3.38[b]	1.57, 1.55, 1.50	1.54
	1.09[b]	0.487, 0.487, 0.487	0.487
	0.39[b]	0.155, 0.147, 0.152	0.151
4 March 1978	29.7[b]	4.53, 4.63, 4.48	4.55
	22.5[a]	7.23, 7.26	7.25
	17.1[a]	6.52, 6.55, 6.25	6.44
	13.7	5.73, 5.72	5.73
	11.5	4.89, 4.59, 4.75	4.74
	6.54	2.86, 2.88, 2.82	2.85
	3.55	1.39, 1.38, 1.38	1.38
	1.35	0.568, 0.580, 0.568	0.572
	0.525	0.215, 0.217, 0.212	0.215

All absorbance readings are corrected to 1.0-cm path length.
a. Not used in least-squares linear regression for combined line.
b. Maximum color appeared before 1 minute.

TABLE B-2. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF CHLORINE DIOXIDE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE (Data Collected on 4 March 1978)

Conc. mg/L ClO_2	Amount KI		
	3 mg	10-18 mg	60 mg
	Absorbance at 1 Minute		
34.4	9.94	8.62	4.18
29.7	9.81	9.23	4.59[a]
22.5	9.74	7.06	3.38[a]
17.1	9.02	7.14	4.28[a]
13.7	7.34	5.52	1.37[a]
11.5	6.00	4.48	1.43[a]
6.54	3.33	3.16	1.52
3.55	1.70	1.50	0.54
1.35	0.630	0.448	0.207
0.525	0.208	0.201	0.070
	Absorbance, Maximum		
34.4	9.95	9.62	8.05
29.7	9.83	9.52	8.07[a]
22.5	9.74	8.28	7.46[a]
17.1	9.02	8.27	7.20[a]
13.7	7.35	6.83	4.05[a]
11.5	6.00	5.66	4.12[a]
6.54	3.34	3.25	3.09
3.55	1.71	1.64	1.39
1.35	0.630	0.604	0.510
0.525	0.209	0.201	0.179

All absorbance readings are corrected to 1.0-cm path length.
a. Not used in least-squares linear regression.

TABLE B-3. FADING OF THE COLOR PRODUCED AT 530 nm BY VARIOUS CONCENTRATIONS OF CHLORINE DIOXIDE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE

Conc. mg/L ClO_2	Absorbance 1 Min	Absorbance 5 Min	Δ	% Decrease
		FACTS II		
34.4	Maximum color at 10 seconds			
29.7	4.79	0.0	4.79	100.0
22.5	7.56	4.25	3.31	43.8
17.1	6.61	4.37	2.24	33.9
13.7	5.86	4.05	1.81	30.9
11.5	4.83	3.84	0.99	20.5
6.54	2.90	2.48	0.42	14.5
3.55	1.39	1.22	0.17	12.2
1.35	0.577	0.514	0.063	10.9
0.525	0.216	0.187	0.029	13.4
		FACTS II Modified (3 mg KI)		
34.4	9.95	8.87	1.08	10.9
29.7	9.83	8.29	1.54	15.7
22.5	9.74	8.93	0.81	8.3
17.1	9.02	7.67	1.35	15.0
13.7	7.35	6.27	1.08	14.7
11.5	6.00	5.72	0.28	4.7
6.54	3.34	3.33	0.01	0.0
3.55	1.71	1.69	0.02	1.2
1.35	0.630	0.614	0.016	2.5
0.525	0.209	0.197	0.012	5.7

All absorbance readings are corrected to 1.0-cm path length.

TABLE B-4. COLOR DEVELOPMENT OF VARIOUS CONCENTRATIONS OF CHLORINE DIOXIDE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE

Date	Conc. mg/L ClO_2	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
4 December 1977 (Selected conc.)	36.9	--[a]	2.25	--[a]	0.0		
		--	2.30	--	0.0		
	20.2	6.70	6.67	--	--	--	--
		6.85	6.65	--	--	--	4.22
		6.60	6.37	--	--	--	--
	12.6[b]	--	4.85	--	--	--	3.62
	9.72	3.85	3.77	--	--	--	--
		3.87	3.82	--	--	--	--
		3.99	3.92	--	--	--	--
		3.87	3.82	--	--	--	2.77
	1.66[b]	0.695	0.692	--	--	--	0.597
11 December 1977 (Selected conc.)	20.8	6.80	6.50	--	--	--	3.52
		6.65	6.45	--	--	--	--
		6.77	6.47	--	--	--	--
	14.0	5.77	5.70	--	--	--	--
		5.77	5.70	--	--	--	4.37
	8.64	3.87	3.82	--	--	--	--
		3.75	3.67	--	--	--	--
		3.72	3.67	--	--	--	3.05
	4.13	1.67	1.66	--	--	--	--
		1.65	1.65	--	--	--	0.452
		1.63	1.62	--	--	--	--
17 December 1977	23.4	6.32	6.04	--	--	--	--
		6.42	6.19	--	--	--	--
		--	6.16	--	--	--	2.37
		6.64	6.30	--	--	--	2.68
	19.1	6.98	6.82	--	--	--	--
		7.20	7.08	--	--	--	4.53
	14.0	5.95	5.82	--	--	--	--
		5.95	5.82	--	--	--	4.37

TABLE B-4 (Continued)

Date	Conc. mg/L ClO_2	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
	13.7	5.89	5.72	--	--	--	--
		5.77	5.67	--	--	--	3.72
	10.1	4.45	4.40	--	--	--	--
		4.47	4.42	--	--	--	2.97
	7.48	3.47	3.45	--	--	--	--
		3.42	3.39	--	--	--	2.62
	3.38	1.57	1.55	--	--	--	--
		1.52	1.50	--	--	--	1.12
	1.09	4.92	4.87	--	--	--	--
		4.95	4.87	--	--	--	4.22
	0.385	0.150	0.147	--	--	--	--
		0.152	0.152	--	--	--	0.127
4 March 1973	29.7	4.74	4.53	2.97	1.46	0.40	0.0
		4.85	4.63	2.92	1.46	0.47	0.0
		4.77	4.48	2.70	1.24	0.28	0.0
	17.1	6.70	6.52	5.93	5.26	4.80	4.43
		6.70	6.55	5.82	5.36	4.95	4.54
		6.44	6.25	5.51	4.81	4.46	4.13
	13.7	5.87	5.73	5.27	4.88	4.41	4.15
		5.85	5.72	5.24	4.82	4.28	3.94
	11.5	4.98	4.89	4.57	4.34	4.15	4.00
		4.69	4.59	4.28	4.02	4.84	3.68
		4.83	4.75	4.43	4.19	3.98	3.85
	6.54	2.91	2.86	2.72	2.63	2.55	2.49
		2.93	2.88	2.75	2.64	2.57	2.52
		2.87	2.82	2.69	2.59	2.50	2.44
	3.55	1.40	1.39	1.33	1.29	1.25	1.22
		1.38	1.38	1.33	1.29	1.25	1.22
		1.39	1.38	1.32	1.28	1.24	1.21

TABLE B-4 (Continued)

Date	Conc. mg/L ClO_2	Absorbance 45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
	1.35	0.574	0.568	0.548	0.532	0.519	0.508
		0.585	0.580	--	--	--	0.525
		0.572	0.568	--	--	--	0.508
	0.525	0.216	0.215	0.207	0.200	--	0.188
		0.218	0.217	0.209	0.202	0.196	0.191
		0.214	0.212	--	--	--	0.183

a. Not observed.
b. Additional samples at each concentration were used but were not followed for 5 minutes.

TABLE B-5. COLOR DEVELOPMENT OF VARIOUS CONCENTRATIONS OF CHLORINE DIOXIDE IN AQUEOUS SOLUTIONS USING THE MODIFIED FACTS II PROCEDURE USING 3 mg KI

Date	Conc. mg/L ClO_2	Absorbance					
		45 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
4 March 1978	34.4	9.66	9.68	9.64	9.56	9.43	9.39
		9.88	9.87	9.85	9.67	9.16	8.66
		10.0	10.0	9.96	9.63	9.23	9.08
	29.7	9.83	9.82	9.71	9.57	9.38	8.88
		9.75	9.72	9.55	8.69	8.19	7.70
		9.92	9.89	9.81	9.24	8.69	8.31
	22.5	9.64	9.69	9.52	9.35	9.08	8.80
		9.74	9.78	9.78	9.32	9.15	9.06
	17.1	8.98	9.00	8.94	8.68	8.35	8.00
		8.88	9.00	8.94	8.44	7.95	7.46
		9.06	9.05	8.95	8.65	8.04	7.55
	13.7	7.31	7.38	7.32	6.87	6.34	6.07
		7.31	7.30	7.12	6.93	6.73	6.44
	11.5	6.04	6.07	6.03	6.01	5.93	5.87
		5.97	5.99	5.97	5.86	5.84	5.64
		5.93	5.93	5.91	5.78	5.76	5.65
	6.54	3.33	3.33	3.30	3.29	3.31	3.33
		3.32	3.32	3.34	3.30	3.25	3.22
	3.55	1.74	1.73	1.73	1.72	1.72	1.71
		1.73	1.72	1.74	1.73	1.73	1.73
		1.69	1.69	1.68	1.68	1.66	1.66
		1.69	1.68	1.68	1.67	1.66	1.65
	1.35	0.629	0.627	0.618	0.613	0.608	0.612
		0.630	0.630	0.623	0.618	0.616	0.614
		0.632	0.632	0.626	0.622	0.618	0.615
	0.525	0.210	0.209	0.205	0.202	0.200	0.198
		0.207	0.207	0.203	0.200	0.198	0.195
		0.210	0.209	0.206	0.203	0.200	0.197

APPENDIX C

Experimental Data for the Development of the FACTS Procedure for the Determination of Iodine in Aqueous Solution

TABLE C-1. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF IODINE IN AQUEOUS SOLUTION USING THE FACTS II PROCEDURE

Date	Conc. mg/L I_2	Absorbance 1 Min	Average
24 October 1977	42.7	9.87, 9.77	9.82
	31.9	9.83, 9.73, 9.75	9.77
	23.1	7.73, 7.72	7.73
	18.6	6.11, 6.12	6.12
	14.2	4.84, 4.88	4.86
	10.8	3.28, 3.27	3.28
	6.82	2.00, 2.01	2.01
	5.31	1.68, 1.68	1.68
	4.13	1.09, 1.09	1.09
25 October 1977	55.1	9.68, 9.71, 9.61, 9.65, 9.96	9.65
	36.6	9.57, 9.51	9.54
	35.7	9.45, 9.60, 9.40	9.48
	29.9	9.04, 9.05, 8.90, 9.21	9.05
	24.51	7.73, 7.79	7.76
	7.22	2.15, 2.16, 2.17	2.16
	5.27	1.50, 1.49	1.50
26 October 1977	56.4	9.89, 9.70, 9.78	9.79
	46.6	9.74, 9.75, 9.56, 9.72	9.69
	38.9	9.59, 9.64, 9.65	9.63
	33.0	9.56, 9.45, 9.59	9.53
	30.8	9.30, 9.47, 9.33	9.37
	24.4	7.45, 7.40	7.43
	22.1	7.15, 7.05, 7.02	7.07
	17.2	5.70, 5.76	5.73
	14.0	4.20, 4.20	4.20
	5.56	1.54, 1.56	1.55

All absorbance readings are corrected to 1.0-cm path length.

TABLE C-2. ABSORBANCE AT 530 nm FOR THE REACTION OF VARIOUS CONCENTRATIONS OF IODINE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE WITH DILUTION

Date	Conc. mg/L I_2	Absorbance 1 Min	Average
8 August 1977	41.3	9.34, 9.32	9.33
	20.0	5.99, 6.06, 5.97	6.01
	16.11	4.84, 4.85	4.85
	10.2	3.00, 3.01	3.01
	4.13	1.07, 1.07	1.07
	0.480	0.080, 0.081	0.081
	0.122	0.012, 0.012	0.012
9 August 1977	48.9	9.05, 9.08	9.07
	46.8	9.28, 9.16, 9.28	9.24
	37.0	9.22, 9.24	9.20
	36.3	9.21, 9.20	9.21
	32.2	8.60, 8.48, 8.37, 8.39	8.46
	26.2	7.21, 7.11, 6.91, 6.99	7.05
	22.3	6.36, 6.43, 6.38	6.39
	14.4	3.98, 3.94, 3.92	3.94
	9.60	2.52, 2.51	2.51
	6.54	1.71, 1.65, 1.65	1.67
20 August 1977	47.0	8.70, 8.87, 8.89	8.82
	39.6	8.87, 8.69, 8.85	8.80
	36.5	8.87, 8.75, 8.83	8.82
	25.3	7.15, 7.19	7.17
	19.2	5.74, 5.72	5.73
	15.5	4.01, 3.97, 3.97	3.98
	9.36	3.20, 3.13, 3.13	3.15
	8.35	2.37, 2.35, 2.39	2.37
	4.06	1.03, 1.03	1.03

All absorbance readings are corrected to 1.0-cm path length.

TABLE C-3. FADING OF THE COLOR PRODUCED AT 530 nm BY VARIOUS CONCENTRATIONS OF IODINE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE

Date	Conc. mg/L I_2	Absorbance 1 Min	Absorbance 5 Min	% Decrease
24 October 1977	42.7	1.09	1.04	15.5
	31.9	9.77	7.86	19.5
	23.1	7.73	6.32	18.2
	14.2	4.86	4.08	16.0
	10.8	3.28	3.00	8.5
	6.82	2.01	1.88	6.5
	5.31	1.68	1.59	5.4
	4.13	1.09	1.04	4.7
25 October 1977	55.1	9.65	8.29	14.1
	36.6	9.54	4.89	48.7
	35.7	9.48	5.40	43.0
	29.9	9.05	5.55	38.7
	24.5	7.76	4.40	43.3
	7.22	2.16	1.99	7.9
	5.27	1.50	1.41	6.0
26 October 1977	56.4	9.79	8.57	12.5
	46.6	9.69	6.60	31.9
	38.9	9.63	5.77	40.0
	33.0	9.53	6.20	35.0
	30.8	9.37	5.51	41.2
	24.4	7.43	4.96	33.2
	22.1	7.07	4.81	32.0
	17.2	5.73	5.33	7.0
	14.0	4.20	3.85	8.3
	5.56	1.55	1.41	9.0

All absorbance readings are corrected to 1.0-cm path length.

TABLE C-4. FADING OF THE COLOR PRODUCED AT 530 nm BY VARIOUS CONCENTRATIONS OF IODINE IN AQUEOUS SOLUTIONS USING THE FACTS II PROCEDURE WITH DILUTION

Date	Conc. mg/L I_2	Absorbance 1 Min	Absorbance 5 Min	% Decrease
8 August 1977	41.3	9.33	7.30	21.8
	20.2	6.01	5.55	7.6
	16.11	4.85	4.60	5.1
	10.2	3.00	2.93[a]	2.5[a]
	4.13	1.07	--[a]	--[a]
	0.480	0.081	--[a]	--[a]
	0.122	0.012	--[a]	--[a]
9 August 1977	36.3	9.21	3.08[a]	66.5[a]
	32.2	8.46	--	--
	26.2	7.05	3.48[a]	50.7[a]
	22.3	6.39	--	--
	14.4	3.94	3.89[a]	1.3[a]
	9.60	2.51	--	--
	6.54	1.67	1.62	2.9
20 August 1977	47.0	8.82	4.74	46.3
	39.6	8.80	5.18	41.2
	36.5	8.82	6.11	30.7
	25.3	7.17	4.04	43.7
	19.2	5.37	3.74	34.7
	15.5	3.98	2.80	29.6
	9.36	3.15	2.86	9.6
	8.35	2.37	2.33[a]	1.7[a]
	4.06	1.21	--[a]	--[a]

All absorbance readings are corrected to 1.0-cm path length.
a. Not observed.

TABLE C-5. COLOR DEVELOPMENT OF VARIOUS CONCENTRATIONS OF IODINE IN REACTION WITH FACTS II PROCEDURE

Date	Conc. mg/L I_2	Absorbance 1 Min	2 Min	3 Min	4 Min	5 Min
24 October 1977	42.7	9.87	--[a]	--	--	--
		9.77	9.72	9.44	9.00	8.30
	31.9	9.83	--	--	--	--
		9.73	--	--	--	7.86
		9.75	--	--	--	--
	23.1	7.73	--	--	--	--
		7.72	7.30	6.96	6.80	6.32
	14.2	4.84	--	--	--	--
		4.88	4.64	4.43	4.30	4.08
	10.8	3.28	--	--	--	--
		3.27	3.20	3.12	3.06	3.00
	6.82	2.00	--	--	--	--
		2.01	1.99	1.97	1.92	1.88
	5.31	1.68	--	--	--	--
		1.68	1.64	1.63	1.60	1.59
	4.13	1.09	--	--	--	--
		1.09	1.07	1.06	1.05	1.04
25 October 1977	55.1	9.71	--	--	--	8.42
		9.65	--	--	--	8.15
	36.6	9.57	--	--	--	--
		9.51	9.08	7.30	5.94	4.89
	35.7	9.45	--	--	--	--
		9.40	--	--	--	--
		9.60	8.70	7.30	6.40	5.40
	29.9	9.05	--	--	--	--
		9.04	--	--	--	--
		9.21	8.12	7.30	6.24	5.51
	24.5	7.73	6.86	6.18	4.96	4.40
		7.79	--	--	--	--

TABLE C-5 (Continued)

Date	Conc. mg/L I_2	Absorbance 1 Min	2 Min	3 Min	4 Min	5 Min
	7.22	2.15	--	--	--	--
		2.16	2.11	2.08	2.04	2.01
		2.17	2.11	2.08	2.04	1.97
	5.27	1.50	--	--	--	--
		1.49	1.48	1.44	1.41	1.41
26 October 1977	56.4	9.89	--	--	--	--
		9.70	--	--	--	--
		9.78	--	--	--	8.57
	56.6	9.74	--	--	--	--
		9.72	--	--	--	--
		9.56	8.96	8.25	7.48	6.60
	38.9	9.59	--	--	--	--
		9.64	--	--	--	--
		9.65	--	--	--	--
	33.0	9.56	--	--	--	6.20
		9.45	--	--	--	--
		9.59	--	--	--	--
	30.8	9.47	--	--	--	--
		9.30	--	--	--	--
		9.33	8.42	7.33	6.47	5.51
	24.4	7.45	--	--	--	--
		7.40	7.06	6.26	5.53	4.96
	22.1	7.05	--	--	--	--
		7.15	--	--	--	--
		7.02	--	--	--	4.81
	17.2	5.70	--	--	--	--
		5.76	5.64	5.46	5.40	5.33
	14.0	4.20	--	--	--	--
		4.20	4.14	3.90	3.87	3.85
	5.56	1.54	--	--	--	--
		1.56	--	--	--	1.41

a. Not observed.

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DEVELOPMENT OF FACTS PROCEDURES FOR BROMINE, CHLORINE DIOXIDE, --ETC(U)
JUN 80 E E RYAN, W J COOPER, E P MEIER
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TABLE C-6. COLOR DEVELOPMENT OF VARIOUS CONCENTRATIONS OF IODINE WITH THE FACTS II PROCEDURE WITH DILUTION

Date	Conc. mg/L I_2	Absorbance 1 Min	2 Min	3 Min	4 Min	5 Min
8 August 1977	41.3	9.34	--[a]	--	--	--
		9.32	9.08	8.60	8.01	7.30
		9.33	--	--	--	--
	20.0	5.99	--	--	--	--
		5.97	--	--	--	--
		6.06	5.97	5.91	5.76	5.55
	16.1	4.84	4.80	4.73	4.65	4.65
		4.85	--	--	--	4.55
	10.2	3.00	3.00	2.99	2.95	2.93
		3.10	--	--	--	2.94
	Lower concentrations not followed for 5 minutes					
9 August 1977	36.3	9.21	--	--	--	--
		9.20	--	--	--	3.08
	26.2	1.44	--	--	--	--
		1.38	--	--	--	3.48
	14.4[b]	3.98	--	--	--	3.89
	6.54[b]	1.65	--	--	--	1.62
20 August 1977[b]	47.0	8.70	--	--	--	4.74
	39.6	8.87	--	--	--	5.18
	36.5	8.83	--	--	--	6.11
	25.3	7.19	--	--	--	4.04
	19.2	5.74	--	--	--	3.74
	15.5	3.97	--	--	--	2.80
	9.36	3.20	--	--	--	2.86
	8.35	2.37	--	--	--	2.33

a. Not observed.
b. Additional samples at each concentration were used but were not followed for 5 minutes.

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