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2.8 | 2.5

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3.6

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COMPARISON OF FACTS AND DPD-STEADIFAC PROCEDURES FOR
FREE AND COMBINED CHLORINE IN AQUEOUS SOLUTION

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FINAL REPORT

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In a continuing effort to develop a superior colorimetric test procedure for determining free available chlorine in aqueous solution, a study was designed to compare the FACTS (Free Available Chlorine Test with Syringaldazine) with the recently modified DPD procedure, DPD-STEADIFAC. It was shown that the DPD-STEADIFAC and a minor modification are more specific for free chlorine in the presence of mono- and dichloramine than the DPD procedure. The DPD and DPD-STEADIFAC Modified procedure were shown to have comparable accuracy and

20. Abstract (continued)

and precision. All of the test procedures showed intrusion of NCl_3 into the free chlorine reading. The lower limit of detection for the FACTS[3] and DPD procedures were 0.014 and 0.021 mg/L as Cl_2, respectively.

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EXECUTIVE SUMMARY

In a continuing effort to develop a superior colorimetric test procedure for determining free available chlorine in aqueous solution, a study was designed to compare the FACTS (Free Available Chlorine Test with Syringaldazine) with the recently modified DPD procedure, DPD-STEADIFAC. It was shown that the DPD-STEADIFAC and a minor modification are more specific for free chlorine in the presence of mono- and dichloramine than the DPD procedure. The DPD and DPD-STEADIFAC Modified procedure were shown to have comparable accuracy and precision. All of the test procedures showed intrusion of NCl_3 into the free chlorine reading. The lower limit of detection for the FACTS and DPD procedures were 0.014 and 0.021 mg/L as Cl_2, respectively.

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INTRODUCTION

Free Available Chlorine Test with Syringaldazine (FACTS) has been shown to be free of interferences from mono- and dichloramine[1-3] in the concentrations normally encountered in water disinfected with chlorine. N,N-diethyl-p-phenylenediamine (DPD) was shown to be subject to interferences from mono- and dichloramine.[2,4-6] A recent modification to the DPD procedure, DPD-STEADIFAC, has been reported to reduce the interferences of mono- and dichloramine.[7-9] This modification uses the addition of thioacetamide (immediately after DPD indicator) to quench the reaction of DPD with combined chlorine. This allows the DPD to react immediately with free available chlorine (fast reaction) but quenches the slower reactions of DPD with combined chlorine. Additional studies are needed to determine if the DPD-STEADIFAC procedure is an improvement over the DPD-glycine approach.[10] An acceptable method would show no response to mono- or dichloramine, yet maintain desirable accuracy and precision limits for free available chlorine (FAC).

In comparing the DPD and FACTS procedures, it has been suggested that FACTS did not respond to chloramines because the sensitivity is not low enough to detect small breakthroughs observed with the DPD method.[7] The FACTS procedures were designed for a range of 0 to 10 mg/L as Cl_2. As a result, the FACTS II procedure (as used in a prototype field kit) has a lower detection limit of approximately 0.2 mg/L as Cl_2. The laboratory procedures are more sensitive than the field procedures that use a color comparator.

An accurate determination of the sensitivity of the FACTS procedure has not been made, nor has its sensitivity been compared in the laboratory to that of the DPD procedure. The molar absorptivities of the colored reaction product for both the FACTS and DPD procedures should be determined in the laboratory to aid in comparing the sensitivities of these two methods. Regardless of the relative sensitivities of the two methods, significant interferences from combined chlorine have been observed with the DPD procedures. False positives as high as 1 mg/L as Cl_2 were observed with the DPD test; however, the FACTS test with the same test solutions showed no false positives.

During initial development of the FACTS procedure, trichloramine was considered to be of little importance in either water or wastewater treatment, and was not tested for its effect upon the FACTS analysis. Recent studies indicate that the FACTS procedure will give a positive response to solutions of trichloramine.[7] This has been confirmed in our laboratory in which it was determined that both DPD and FACTS were subject to a positive interference from trichloramine.

Trichloramine is explosive and must be prepared in solution. Several methods for the preparation of trichloramine[11-13] are found in the literature; however, experience has shown that aqueous solutions derived from

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these procedures may not yield solutions free of free available chlorine. Additional effort is required to determine if it is possible to prepare pure aqueous solutions of trichloramine. Such solutions would be helpful in obtaining accurate data on the effect of NCl_3 on chlorine test procedures and in determining its stability at pH levels normally encountered in water treatment.

OBJECTIVES

The objectives of this study were:

1. To determine whether the DPD-STEADIFAC procedure eliminates interferences from mono- and dichloramine in the free chlorine determination.

2. To compare the DPD-STEADIFAC and DPD-STEADIFAC Modified procedures with respect to detection of FAC.

3. To determine the stability of the color formation of the DPD, DPD-STEADIFAC, and DPD-STEADIFAC Modified procedures.

4. To determine the stability of the thioacetamide solution used in the DPD-STEADIFAC test procedure.

5. To compare the theoretical detection limit of the FACTS and DPD methods for FAC.

6. To obtain data on accuracy and precision of the DPD-STEADIFAC test procedure in the determination of FAC.

7. To study the feasibility of preparing pure aqueous solutions of trichloramine in the absence of dichloramine for the determination of the stability of NCl_3 within a pH range of 6-10.

8. To determine the effect of trichloramine on the DPD, DPD-STEADIFAC Modified, and FACTS test procedures.

METHODS AND MATERIALS

Unless otherwise stated, all reagents used were Certified ACS Reagent Grade. The following reagents and procedures were used for this study.

Chlorine Demand-Free Water. Sufficient Clorox^R was added to distilled water to yield a free available chlorine residual concentration of approximately 1 mg/L as Cl_2 after standing overnight. The solution was then dechlorinated by exposure to sunlight for several days until no positive indication of residual chlorine was given by the FACTS-KI total available

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chlorine test. The resulting demand-free water was used to prepare chlorine solutions for this study.

Demand-Free Glassware. The glassware in this study was treated with cleaning solution (35g $Na_2Cr_2O_7$/L of H_2SO_4 conc.) and rinsed with 15% HCl. The glassware was then soaked in chlorinated water to remove any chlorine demand and rinsed with demand-free water before use. Some glassware was cleaned in this manner, rinsed with distilled water, and oven-dried for storage until used.

DPD. Fast-dissolving tablets (LaMotte-Palin DPD Chlorine #1R, LaMotte Chemical, Chestertown, MD 21620) were used for the DPD and DPD-STEADIFAC procedures in this study.

DPD Procedure. The following DPD procedure was used:

1. Rinse a 12-mL test tube with 10 mL of test solution.

2. Add 10 mL of test solution to the tube.

3. Add a DPD #1 tablet and invert once to mix.

4. Read the color immediately with a color comparator or a spectrophotometer (λ_{max} = 515 nm) and record the reading as concentration or absorbance, respectively.

DPD-STEADIFAC Procedure. The following procedure was used:

1. Add one drop of 0.25% thioacetamide solution (2.5 gm/L demand-free water) and 10 mL of test solution to a 12-mL test tube. Invert to mix and discard contents.

2. Add 10 mL of test solution to the tube.

3. Add a DPD #1 tablet and invert to mix.

4. Immediately add one drop of 0.25% thioacetamide solution and invert once to mix.

5. Read the color immediately with a color comparator or a spectrophotometer (λ_{max} = 515 nm) and record the reading concentration or absorbance, respectively.

It has been determined, through preliminary testing with this DPD-STEADIFAC procedure, that the initial tube-rinse with 0.25% thioacetamide solution yields low results in free available chlorine analysis. Deletion of the thioacetamide in the initial tube-rinse should give more

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accurate free available chlorine readings. The DPD-STEADIFAC Modified procedure did not utilize thioacetamide solution for step 1.

FACTS Reagent. FACTS indicator was prepared by dissolving, with sonification, 115 mg syringaldazine (Aldrich Chemical #17,753-9, 99+%) in 1 liter of 2-propanol.

FACTS Buffer. The FACTS buffer was prepared by mixing equal volumes of 0.5 M sodium phosphate dibasic (Na_2HPO_4) and 0.5 M potassium phosphate monobasic (KH_2PO_4).

FACTS Procedure. The following FACTS procedure was used:

1. Rinse a 12-mL test tube with 5 mL of test solution.

2. Add 5 mL of test solution.

3. Add 0.2 mL of 0.5 M phosphate buffer (pH = 6.5).

4. Add 2 mL of FACTS indicator and invert twice to mix.

5. Read the color immediately with a color comparator or a spectrophotometer (λ_{max} = 530 nm) and record the reading as concentration or absorbance, respectively.

Iodometric Analysis. The iodometric titration procedure as presented in Standard Methods[14] was used to estimate the free available chlorine concentrations in the stock chlorine solutions used for sample preparation.

Amperometric Analysis. Amperometric titration was used as the reference method for low concentrations (up to 2 mg/L) of FAC and combined chlorine.[14] A Fischer and Porter Model 17T1010AJ amperometric titrator with phenylarsene oxide (0.00564N) as the titrant was employed. The following amperometric titration procedures were used:

1. FAC: One eyedropper of pH 7.0 buffer was added to a 200-ml test sample. With the titrator switch in the "free" position, the solution was titrated to the first endpoint (titration #1).

2. Monochloramine: The titrator switch was changed to the "total" position. Four drops of 5% potassium iodide (KI) was then added and the solution titrated to the second endpoint (titration #2).

3. Dichloramine: One eyedropper of pH 4.0 buffer and one eyedropper of 5% KI was added to the test solution. The solution was then titrated to the third endpoint (titration #3). The concentrations of the chlorine species were calculated as follows:

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mL titration #1 = free available chlorine (mg/L)

mL titration #2 - mL titration #1 = monochloramine (mg/L)

mL titration #3 - mL titration #2 = dichloramine (mg/L)

DPD ferrous titrimetric method. This titration method as presented in Standard Methods[14] was used to determine FAC and combined chlorine when trichloramine was present.

Stock Chlorine Solutions. These solutions were prepared by the addition of 10 mL Clorox[R] to 1 liter demand-free water to yield approximately 270 mg/L free available chlorine.

Monochloramine. Aqueous samples were prepared using the following procedure:

To a half-liter of stock chlorine solution (26 mL Clorox[R]/L) buffered to pH 8.0 with 0.5 M $NaHCO_3$ was added 500 mL 0.55 M NH_4Cl. The pH of this solution was maintained at approximately 8.0 with small additions of 1 N sodium hydroxide. This procedure formed approximately 200 mg/L monochloramine on contact. To avoid exposure to light, these solutions were stored in low actinic glass bottles and placed in the refrigerator.

Dichloramine. Aqueous samples were prepared using the following procedure:

a. A 50-mg/L monochloramine solution was prepared by appropriate dilution of stock monochloramine.

b. The pH of this solution was then lowered to 4.0 by the addition of concentrated phosphoric acid. Dichloramine was formed within approximately 2 hours. These dichloramine solutions are unstable and were prepared immediately before use.

Trichloramine. (1) Aqueous samples were prepared using the following procedure:

To 100 mL of 3.7×10^{-3} M NH_4Cl in a gas washing bottle was added 100 mL of 1.4×10^{-2} M NaOCl (approximately 10 mL Clorox[R]/L). Each solution was prepared with chlorine demand-free water and adjusted to pH 2.3 with 6N HCl prior to mixing. Indication that NCl_3 had formed immediately was given by a distinctive, irritating odor and was confirmed by an absorption maximum in the ultraviolet at 220 nm. A gas inlet tube, connected to a nitrogen source with tygon tubing, was inserted into the reaction

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bottle. The exit port of the reaction bottle was connected with tygon
tubing to another gas inlet tube. This tube was placed in a 1-liter
brown glass bottle, filled with chlorine demand-free distilled water,
while the bottle was sitting in an ice bath. Nitrogen was then bubbled
through the reaction mixture at a pressure just sufficient for the gas to
break up into small bubbles (10 psi). After 30 minutes, the nitrogen was
no longer added and a spectrophotometric analysis showed a maximum yield
of 13.8 ppm (9.7%) trichloramine. The solution was stored at 0°C until
used. The experimental apparatus is shown schematically in Figure 1.

Trichloramine. (2) Aqueous samples were also prepared using a modifica-
tion of the method of Dennis et al.[13]

To 0.112 g of uracil (1 x 10^{-3} mole) was added 100 mL chlorine
demand-free water, 10 mL pH 7 buffer solution (K_2HPO_4-NaOH), and 22 mL
of 5% NaOCl (1.5 x 10^{-2} mole). NCl_3 was produced according to the
equation:

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| \quad\quad \| \quad\quad + \text{ HOCl} \rightarrow NCl_3\uparrow + CO_2 + Cl_3CCO_2H \\
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\text{O} \quad \text{H} \\
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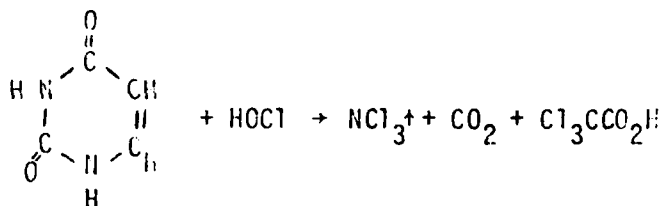
The apparatus used here was identical to that employed in the previous
experiment (see Fig. 1). Nitrogen was bubbled through the reaction mix-
ture at a pressure just sufficient to break up into small bubbles. After
20 minutes, the nitrogen was turned off and a spectrophotometric analysis
showed a maximum yield of 7 mg/L trichloramine. The solution was stored
at 0°C until used.

Decomposition of Trichloramine. Where reaction mixtures at pH 2 were
studied, the reaction was carried out in brown glass bottles. Otherwise,
trichloramine was collected in 1-liter brown glass bottles, warmed to
room temperature, and adjusted to the appropriate pH as follows: pH 6, 7,
and 8 with 0.1 M KH_2PO_4 and 0.1 M NaOH; pH 9 with 0.025 $Na_2B_4O_7$.10 H_2O
(Borax) and 0.1 M HCl; pH 10 with 0.05 M $NaHCO_3$ and 0.1 M NaOH. During
the runs, these bottles were kept in the dark except when samples were
removed. Each sample was taken with a fresh 5-mL, acid-washed, rinsed
and dried pipette. Half the sample was used to rinse the 1-cm quartz
cell. After discarding the first portion, the remainder was placed in the
cell and the spectrum from 250 to 200 nm was observed.

Spectrophotometers. A Beckman ACTA CV, UV-Visible spectrophotometer
was used for all spectrophotometric determinations.

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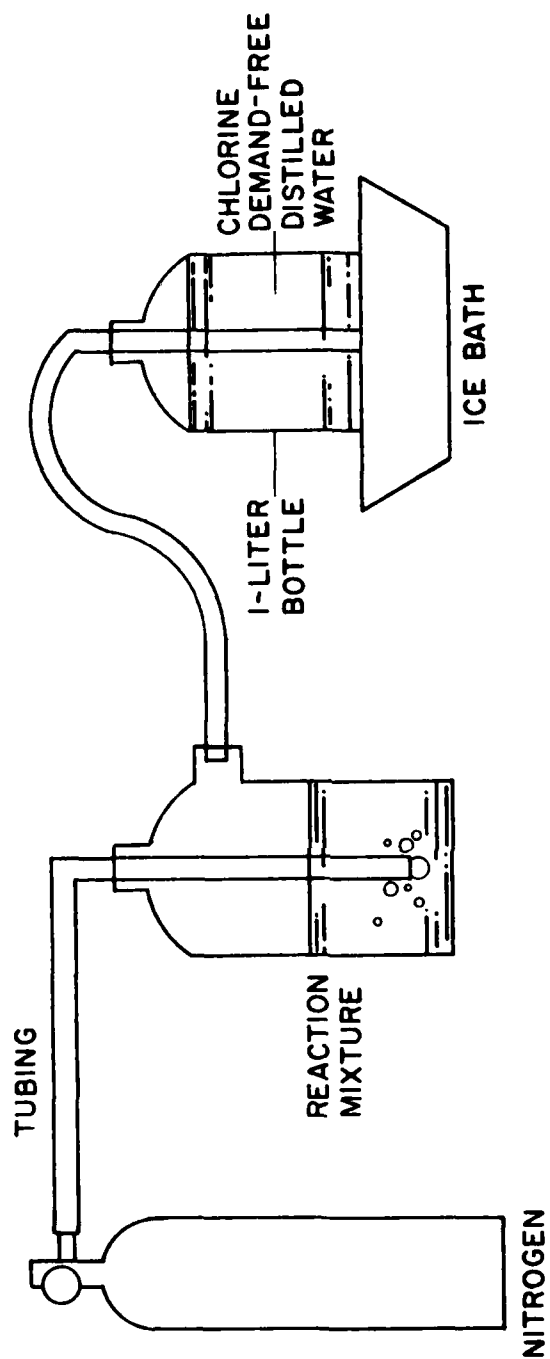
Figure 1. Apparatus for Preparation and Collection of Nitrogen Trichloride.

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RESULTS AND DISCUSSION

Combined Chlorine. The initial objective of the study was to determine whether the DPD-STEADIFAC procedure eliminated the interferences from monochloramine and dichloramine that had been observed previously with the DPD procedure when determining free chlorine in the presence of combined chlorine. The concentrations of combined chlorine that yield a positive response with the DPD procedure have been identified in earlier work.[4-6,10] The response of the DPD-STEADIFAC procedure to the combined chlorine concentrations was determined. The data obtained were used to evaluate the DPD-STEADIFAC specificity and to compare it to the DPD procedure. Ten tests were performed at each specified concentration of combined chlorine. Amperometric titration was used as the reference method to determine combined and free available chlorine in the test samples. The FACTS procedure was also tested with these solutions to provide a valid comparison of the colorimetric methods available.

The effect of monochloramine on the FACTS procedure is shown in Table 1. The FACTS procedure shows no initial interference from monochloramine at concentrations up to 24 mg/L. However, if the time elapsed between mixing the reagents and reading the color produced on the color comparator is 5 minutes or greater, false positives are observed at monochloramine concentrations of 13.2 and 24 mg/L as Cl_2, yielding apparent FAC readings in the range of 0.2 to 0.3 mg/L.

TABLE 1. INTERFERENCE OF MONOCHLORAMINE WITH THE FACTS PROCEDURE
USING SYNTHETIC WATERS

Sample No.	NH_2Cl (mg/L as Cl_2)[a]	Apparent FAC Readings (mg/L as Cl_2)	
		1 min after Mixing	5 min after Mixing
1	1.2	0	0
2	3.5	0	0
3	6.4	0	0
4	13.2	0	0.19
5	24.2	0	0.16

a. As determined by amperometric titration.

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The effect of monochloramine on the DPD procedure is shown in Table 2. At the lowest concentration of monochloramine tested, 1.2 mg/L, apparent FAC readings of 0.4 mg/L were obtained with the procedure when the time elapsed between mixing reagents and reading the color produced on the color comparator was 5 minutes. At the 6.4 and 13.2 mg/L monochloramine levels, breakthrough was immediate, yielding apparent FAC readings of 0.2 and 0.5 mg/L, respectively. At the highest monochloramine concentration tested, 24.2 mg/L, breakthrough was immediate, yielding apparent FAC readings of 1.0 to 1.5 mg/L (Fig. 2).

In order to provide a relative measurement of the breakthrough of monochloramine into the free measurement, a percentage figure was obtained by dividing the apparent free available chlorine reading by the known monochloramine tested. These data are presented in Table 2. It can be seen that the percent/minute for the upper three levels of monochloramine agree well at the 1-minute and 5-minute reading. The average percent/ minute breakthrough at the 5-minute reading was 4.48. This is significantly higher than reported by Palin.*

The FACTS procedure showed no interference with a-y of the various dichloramine concentrations tested (none through 20 mg/L as Cl_2) throughout the 5-minute test period.

Dichloramine began to interfere with the DPD procedure at 20 mg/L. If the time elapsed between mixing the reagents and reading the color produced on the color comparator was 5 minutes, breakthrough of monochloramine occurred yielding apparent FAC readings of 0.5 mg/L.

Dichloramine does not produce apparent readings of free chlorine as does equivalent concentrations of monochloramine.

No interference from either NH_2Cl (Table 3) or $NHCl_2$ was observed with the DPD-STEADIFAC or the DPD-STEADIFAC Modified procedure.

It was observed that when solutions of either NH_2Cl or $NHCl_2$ were tested with DPD-STEADIFAC or the DPD-STEADIFAC Modified procedures, the solution became cloudy. This also occurred to a lesser extent with free available chlorine solutions.

Because of the extent of combined chlorine interference in the DPD procedure, it is not suitable to distinguish between free and combined chlorine. Preliminary testing indicates that the DPD-STEADIFAC Modified procedure is free from interferences by combined chlorine. However, the additional step of thioacetamide addition does add to the complexity of the procedure as a laboratory or field test procedure.

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* Personal Communication (possibly Standard Methods).

TABLE 2. INTERFERENCE OF MONOCHLORAMINE WITH THE DPD PROCEDURE IN SYNTHETIC WATERS

Sample No.	NH_2Cl (mg/L as Cl_2)[a]	Apparent Free Available Chlorine FAC Readings				
		1 min after Mixing	% of NH_2Cl	5 min after Mixing	% of NH_2Cl	% of NH_2Cl/min
1	1.2	0	0	0.4	3.3	6.7
2	3.5	0	0	0.8	22.9	4.6
3	6.4	0.2	3.1	1.25	19.5	3.9
4	13.2	0.54	4.0	2.60	19.7	3.9
5	24.2	1.35	5.6	4.0	16.5	3.3

a. As determined by amperometric titration.

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Figure 2.   Interference of Monochloramine on the DPD Procedure
in Synthetic Waters.

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TABLE 3. INTERFERENCE OF MONOCHLORAMINE WITH THE DPD-STEADIFAC MODIFIED
PROCEDURE IN SYNTHETIC WATERS

Sample No.	NH_2Cl (mg/L as Cl_2)[a]	Apparent FAC Readings	
		1 min after Mixing	5 min after Mixing
1	1.2	0	0
2	3.5	0	0
3	6.4	0	C
4	13.2	0	0
5	24.2	0	0

a. As determined by amperometric titration.

DPD-STEADIFAC Procedure vs. DPD-STEADIFAC Modified Procedure. The
second objective of the study was to compare the two procedures, DPD-
STEADIFAC and DPD-STEADIFAC Modified, with respect to detection of FAC.
Three spectrophotometric determinations were made at seven concentrations
of FAC, for each procedure. The stability of the color formed by each
procedure was monitored spectrophotometrically at six concentrations of
FAC for a time period of 5 minutes.

The DPD-STEADIFAC procedure includes the addition of thioacetamide
solution to the test solution in the initial tube-rinse, whereas the
DPD-STEADIFAC Modified procedure deletes thioacetamide in the initial
tube-rinse. Figure 3 is a comparison of Beer's Law plots obtained from
testing solutions of free available chlorine of varying concentrations.
The data are tabulated in Tables 4 and 5 for free DPD-STEADIFAC and DPD-
STEADIFAC Modified procedures, respectively. It was noted that using the
DFD-STEADIFAC procedure at concentrations up to 1 mg/L, no color was
observed in the test solutions.

The line obtained from graphing absorbance values vs. concentration
of free available chlorine is more linear for the DPD-STEADIFAC Modified
procedure than for the DPD-STEADIFAC procedure. This can be explained
by the fact that the thioacetamide added in the modified procedure has
not affected the analysis of free available chlorine and most closely
approximates the results obtained for the DPD procedure with free avail-
able chlorine.
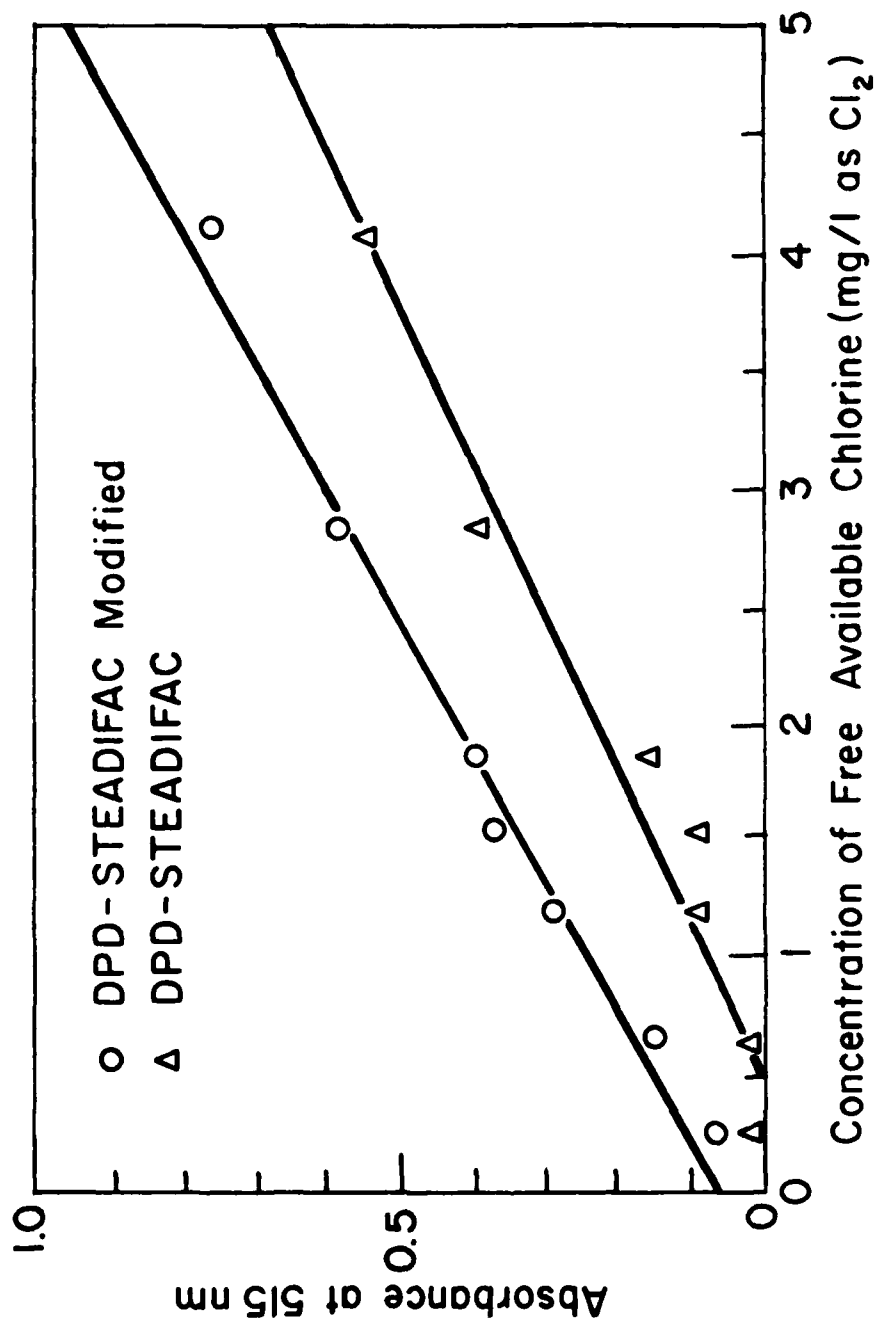
Figure 3. Comparison of Beer's Law Plots for the DPD-STEADIFAC and the DPD-STEADIFAC Modified Procedures.

TABLE 4. BEER'S LAW DATA FOR THE DPD-STEADIFAC PROCEDURE
FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	Absorbance			Average
0.19	0.018	0.012	0.014	0.015
0.61	0.023	0.017	0.028	0.023
1.12	0.073	0.082	0.084	0.080
1.49	0.085	0.086	0.080	0.084
1.81	0.150	0.139	0.164	0.151
2.79	0.368	0.418	0.327	0.394
4.11	0.546	0.606	0.515	0.555

a. As determined by amperometric titration.

TABLE 5. BEER'S LAW DATA FOR THE DPD-STEADIFAC MODIFIED PROCEDURE
FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	Absorbance			Average
0.19	0.070	0.049	0.048	0.055
0.61	0.163	0.125	0.139	0.142
1.12	0.282	0.286	0.294	0.287
1.49	0.432	0.361	0.313	0.369
1.81	0.415	0.382	0.410	0.402
2.79	0.598	0.616	0.576	0.597
4.11	0.780	0.778	0.751	0.770

a. As determined by amperometric titration.

One problem encountered throughout these studies was the inability of some of the DPD tablets to dissolve completely. One minute after the addition of the tablets to the test solution, there were still undissolved tablet fragments. The tablets used were DPD #1 fast-dissolving tablets. If the tablets were allowed to dissolve completely, there might be fading of the color formed within that time period, yielding lower free available chlorine readings. This is discussed in the section on color fading in the DPD, DPD-STEADIFAC, and DPD STEADIFAC Modified procedures.

Color Formation and Stability of the DPD, DPD-STEADIFAC, and DPD-STEADIFAC Modified Procedures. The third objective of the study was to determine the effect of color stability on accuracy. Analytical determinations must produce a color that is stable for a reasonable time period (within 5 minutes).

Tables 6, 7, and 8 tabulate the data for the DPD, DPD-STEADIFAC, and DPD-STEADIFAC Modified procedures, respectively. These data were obtained using free available chlorine concentrations of 0.20 through 9.45 mg/L as Cl_2 in synthetic water. Figure 4 compares the data of all three procedures graphically.

TABLE 6. COLOR FORMATION AND FADING IN SYNTHETIC WATER USING THE DPD PROCEDURE FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	Absorbance		Decrease in Absorbance (%)
	1 min	5 min	
0.20	0.060	0.042	30
0.75	0.218	0.184	15.6
3.79	0.792	0.734	7.3
5.53	0.955	0.868	9.1
7.43	1.077	1.048	2.7
9.45	1.188	1.108	6.7

a. As determined by amperometric titration.

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TABLE 7. COLOR FORMATION AND FADING FOR SYNTHETIC WATER USING
THE DPD-STEADIFAC PROCEDURE FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	Absorbance		Decrease in Absorbance (%)
	1 min	5 min	
0.20	0.036	0.010	72.2
0.75	0.040	0.026	35.0
3.79	0.661	0.583	11.8
5.53	0.885	0.750	15.2
7.43	1.024	0.931	9.1
9.45	1.113	1.062	4.6

a. As determined by amperometric titration.

TABLE 8. COLOR FORMATION AND FADING FOR SYNTHETIC WATER
USING THE DPD-STEADIFAC MODIFIED PROCEDURE
FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	Absorbance		Decrease in Absorbance (%)
	1 min	5 min	
0.20	0.056	0.040	28.6
0.75	0.227	0.196	13.7
3.79	0.824	0.708	14.1
5.53	1.003	0.864	13.9
7.43	1.090	1.052	3.5
9.45	1.122	1.083	3.5

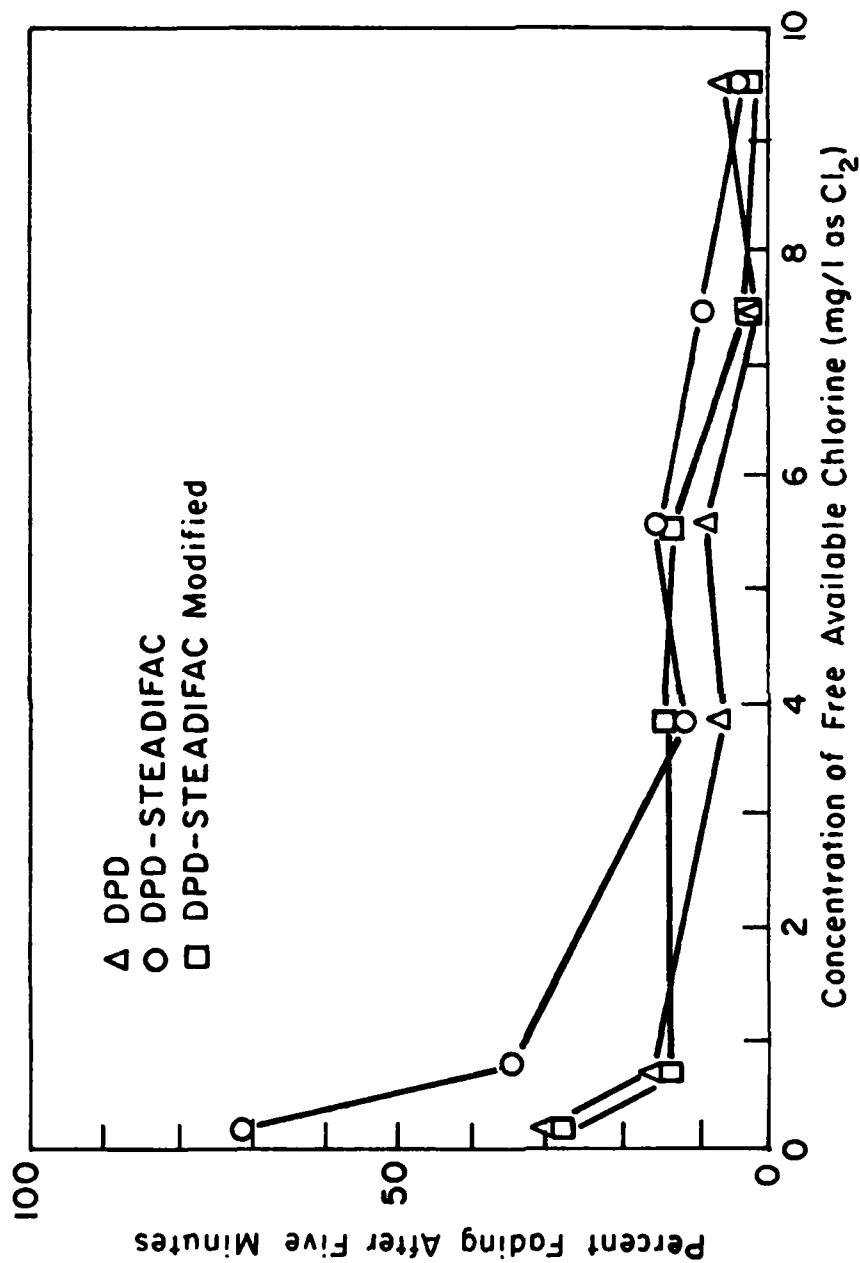a. As determined by amperometric titration.

Figure 4. Comparison of the Fading in Synthetic Waters Using the DPD, DPD-STEADIFAC, and DPD-STEADIFAC Modified Procedures for Free Available Chlorine.

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The results indicated that the DPD and DPD-STEADIFAC Modified procedures showed insignificant fading at low and high concentrations of free available chlorine, as determined spectrophotometrically.

The DPD-STEADIFAC procedure showed more fading at concentrations up to 1 mg/L, after which the fading pattern followed that of the other two procedures. The absolute absorbance at these low concentrations was very low as a result of the reaction of the free chlorine with the thioacetamide.

The fading was proportionally greater at lower concentrations of FAC for all procedures. Whether or not this is an operational problem rests solely on the speed with which determinations are made.

Aging of Thioacetamide Solution in the DPD-STEADIFAC and DPD-STEADIFAC Modified Procedures. The fourth objective of the study was to determine the stability of the thioacetamide solution used in the DPD-STEADIFAC test procedures. Thioacetamide is added in the DPD-STEADIFAC procedures to prevent reaction of DPD with combined chlorine. If the thioacetamide degrades upon aging, it may not produce the desired results and might even increase the false positive response.

The stability of the thioacetamide solution used in the DPD-STEADIFAC and DPD-STEADIFAC Modified procedures was tested during a 4.5-month period (133 days). The DPD procedure was used as a control throughout this period.

Two levels of FAC were tested, approximately 0.4 and 3.0 mg/L as Cl_2. These were used to ascertain the effect of the aging thioacetamide on the free chlorine measurement. The two levels of monochloramine used were approximately 6 and 26 mg/L as Cl_2. Admittedly, the 26 mg/L level is high; however, this level was chosen to stress the thioacetamide and to demonstrate any subtle changes in its ability with age to retard monochloramine intrusion into the free chlorine measurement.

The data obtained for this experiment are summarized in Table 9. The results indicate that within the 4.5-month period, the thioacetamide solution eliminated the intrusion of the monochloramine into the free chlorine fraction.

Throughout the 4.5-month period, no adverse effect was noticed on the measurement of FAC with the DPD-STEADIFAC Modified procedure. During the same time, the DPD-STEADIFAC procedure consistently read zero for the lower FAC concentration of 0.4 mg/L as Cl_2. Experiments should be conducted in order to extend this to a year or more.

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TABLE 9. EFFECT OF AGED THIOACETAMIDE SOLUTIONS ON THE DPD PROCEDURES
FOR THE DETECTION OF FREE AVAILABLE CHLORINE
AND ELIMINATING THE MONOCHLORAMINE INTERFERENCE

FAC Added (mg/L as Cl_2)[a]	FAC Observed (mg/L as Cl_2)	NH_2Cl Added (mg/L as Cl_2)[a]	Apparent FAC Reading	Age of Thioacetamide Solution (days)
DPD Procedure				
0.42	C.50	6.6	0.27	
2.97	3.0	26.32	0.53	
C.39	0.40	6.4	0.20	
3.01	3.0	26.65	0.60	
0.40	0.4C	6.2	0.13	
3.05	2.83	28.65	0.60	
0.45	0.57	6.1	0.10	
2.95	2.80	23.40	0.60	
0.39	C.4C	6.11	0.27	
3.06	3.0	26.12	0.67	
0.39	0.4	6.11	0.20	
3.06	2.8	26.12	0.60	
DPD-STEADIFAC Procedure				
0.36	0	2.83	0	1
3.19	2.7	22.85	0	1
0.41	0	6.11	0	14
2.95	2.3	26.20	0.1	14
0.39	0	5.95	0	29
3.01	2.0	25.60	0	29
0.39	0.4	6.11	0	112
3.06	2.5	26.12	0	112
0.39	0	6.11	0	133
3.06	2.3	26.12	C	133

TABLE 9 (Cont.)

FAC Added (mg/L as Cl_2)[a]	FAC Observed (mg/L as Cl_2)	NH_2Cl Added (mg/L as Cl_2)[a]	Apparent FAC Reading	Age of Thioacetamide Solution (days)
DPD-STEADIFAC Modified Procedure				
0.42	0.60	6.6	0	1
2.97	2.67	26.32	0	1
0.39	0.27	6.4	0	18
3.01	2.87	26.65	0	18
0.40	0.40	6.2	0	30
3.05	3.00	28.65	0	30
0.45	0.50	6.1	0	45
2.95	2.80	23.40	0	45
0.39	0.40	6.11	0	112
3.06	2.80	26.12	0	112
0.39	0.37	6.11	0	133
3.06	3.00	26.12	0	133

a. As determined by amperometric titration.

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<u>Detection Limit of FACTS vs. DPD Test Procedures for Free Available Chlorine.</u> The fifth objective of the study was to determine the theoretical detection limit of the FACTS and DPD test procedures for FAC with the spectrophotometer. The instrumental method, in this case using a spectrophotometer, should be capable of detecting lower concentrations of FAC than the visual method. The instrumental sensitivity is defined as the FAC concentration that produces a signal three times the noise level (background signal) of the instrument. The sensitivity was obtained from the equation for the Beer's Law response observed for each method. Thus, substitution of the absorbance value equivalent to three times the background level observed into the Beer's Law Equation provides a reasonable estimate of the sensitivity for each method.

Seven concentrations of FAC were tested in order to obtain the necessary data to calculate the detection limit of the DPD and FACTS procedures. The results obtained are presented in Table 10 and are plotted in Figures 5 and 6 for DPD and FACTS, respectively.

TABLE 10. DATA FOR BEER'S LAW PLOT FOR THE DPD PROCEDURE AND THE FACTS PROCEDURE IN SYNTHETIC WATER FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	Absorbance			Average
	DPD (515 nm)			
0.203	0.060	0.059	0.055	0.058
0.402	0.085	0.090	0.088	0.088
0.650	0.130	0.132	0.136	0.133
0.780	0.190	0.189	0.203	0.196
1.120	0.230	0.228	0.225	0.228
2.106	0.440	0.425	0.430	0.432
5.530	0.900	0.905	0.909	0.905
7.483	1.200	1.215	1.215	1.210
	FACTS (530 nm)			
0.203	0.090	0.088	0.083	0.087
0.402	0.185	0.186	0.180	0.184
0.650	0.440	0.420	0.438	0.432
0.780	0.490	0.488	0.506	0.495
3.798	3.28	3.24	3.28	3.26[b]
5.530	4.84	4.74	4.74	4.77[b]
7.483	6.62	6.70	6.60	6.64[b]

a. As determined by amperometric titration.
b. These values were obtained using a 0.5-cm spectrophotometric cell. All other values were obtained using 1.0-cm cells.
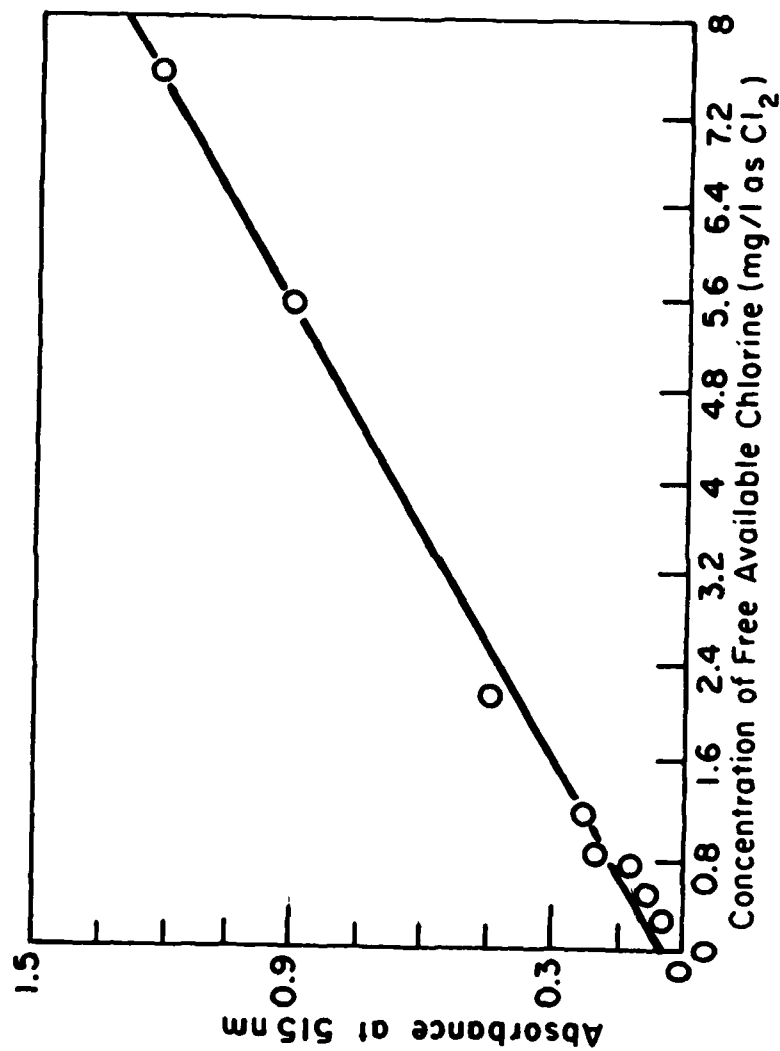
Figure 5. Beer's Law Plot for the DPD Procedure and for Free Available Chlorine in Synthetic Water.
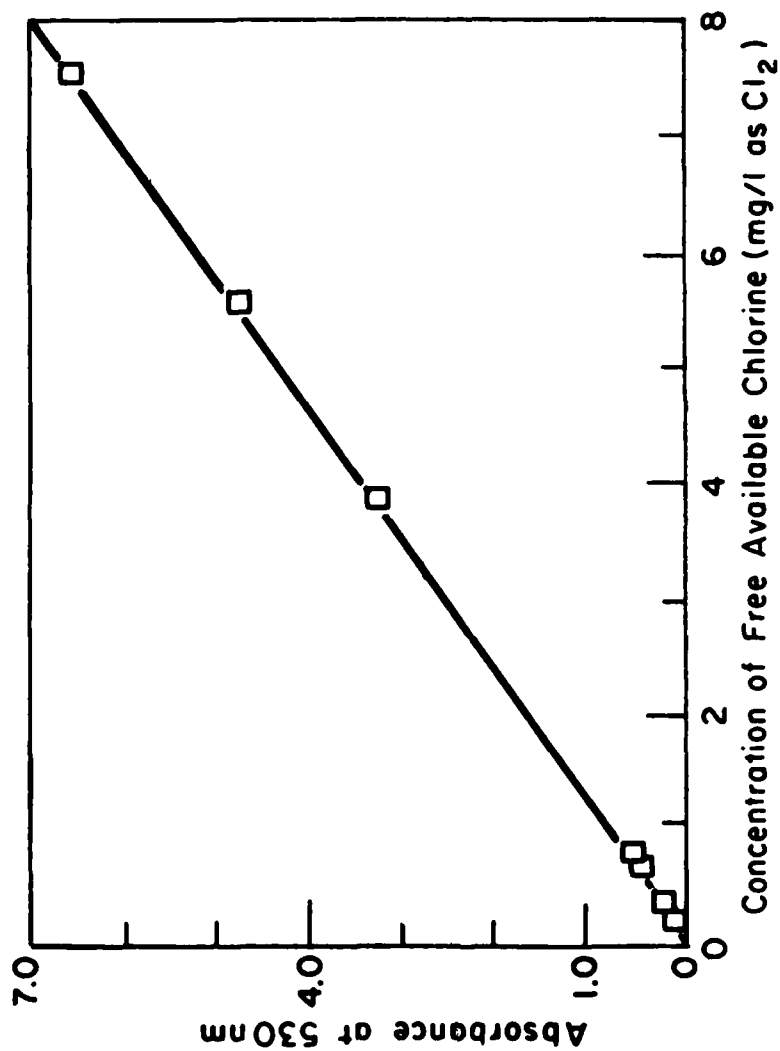
28

Figure 6. Beer's Law Plot for the FACTS Procedure and for Free Available Chlorine in Synthetic Water.

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The following procedure was then used for the numerical determination:

FACTS

$y = mx + b$ (where $b = 0$)
$m = y/x$

$A = ebc$ (where $b = 1$)
$e = A/c$

$A = y$ (absorbance)
$c = x$ (concentration)
then $A/c = y/x$ and $e = m$ (slope of line)

$y_1/x_1 = e$

First convert x values to moles/L. $x = mg/L$. To convert to moles, divide by 1000 mg/g, and then divide by 35 g/mole, which gives the concentration (moles/L).

For y_1/x_1 where $y = 0.037$ and $x = 0.0000058$ moles/L, $e = 1.5 \times 10^4$.

If $e = A/c$, where c is the concentration that will yield three times the background signal of the instrument ($A = 0.006$), then where $e = 1.5 \times 10^4$ and $A = 0.006$, the concentration in moles is equal to $c = A/e$ or 4.0×10^{-7} moles/L or 0.014 mg/L as Cl_2.

DPD

For y_1/x_1 where $y = 0.058$ and $x = 0.0000058$ moles/L, $e = 1.0 \times 10^4$.

If $e = A/c$, where c is the concentration that will yield three times the background signal of the instrument ($A = 0.006$), then where $e = 1.0 \times 10^4$ and $A = 0.006$, the concentration in moles is equal to $c = A/e$ or 6.0×10^{-7} moles/L or 0.021 mg/L as Cl_2.

The data showed that for equal concentration the FACTS procedure resulted in a higher absolute absorbance. This was confirmed by the above calculations, which demonstrated that the theoretical detection limit of the FACTS tests is lower than the DPD test.

Neither procedure resulted in a line that went through zero. In the case of the FACTS, this may be indicative of a small impurity in the 2-propanol. This has been observed in other work carried out in this laboratory and can be corrected by the use of carbon to remove the trace impurities in the 2-propanol. The fact that the DPD resulted in a line that did not go through zero was unexplained.

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Accuracy and Precision. The sixth objective was to obtain data on accuracy and precision of the DPD-STEADIFAC test procedure for FAC analysis. Precision is defined as the reproducibility of a method when it is repeated on a homogeneous sample under controlled conditions. It is best expressed by the standard deviation.

Twenty determinations were made at each of six free available chlorine concentrations with the DPD, DPD-STEADIFAC, and DPD-STEADIFAC Modified procedures. The test solutions were dilutions of Clorox[R] in demand-free water. The results obtained with the DPD procedure were compared with results obtained with the DPD-STEADIFAC and DPD-STEADIFAC Modified procedures.

If the use of thioacetamide does not affect the analysis of free available chlorine, these procedures should yield similar values. The data obtained in measuring test kit precision were also used to determine test kit accuracy. Amperometric titration was used as the reference method for determining the true concentration.

The following expression:

Relative Error = Amperometric Value - Observed Value X 100

was used to compare test kit accuracy. The observed value is the average of the data. The expression:

$$s = \frac{\Sigma(x-x)^2}{n-1} = \frac{1}{n-1} \Sigma X^2 - \frac{1}{n} (\Sigma x)^2$$

will be used to compare test kit precision.

Table 11 is a summary of the accuracy and precision obtained for the DPD procedures. It appears from a comparison of the standard deviation and relative error that the DPD-STEADIFAC Modified procedure is comparable to the DPD procedure and that the DPD-STEADIFAC procedure has a substantially higher relative error associated with it. This was predicted from the outset as a result of the addition of thioacetamide before sample addition.

Preparation of Aqueous Trichloramine. The seventh objective of this study was to explore methods of obtaining pure aqueous solutions of trichloramine. A variety of extraction procedures was applied to trichloramine prepared in aqueous and non-aqueous solutions. The presence of trichloramine was detected spectrophotometrically at 220 nm. A more successful approach was to purge the trichloramine from the reaction mixture with a carrier gas (nitrogen) and bubble it through chlorine demand-free distilled water to recapture it.

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TABLE 11. A SUMMARY OF THE ACCURACY AND PRECISION DATA FOR FIELD TEST KIT DPD PROCEDURES IN SYNTHETIC WATERS FOR FREE AVAILABLE CHLORINE

FAC (mg/L as Cl_2)[a]	DPD			DPD-STEADIFAC Modified			DPD-STEADIFAC		
	Mean	Std. Dev.	Rel. Error	Mean	Std. Dev.	Rel. Error.	Mean	Std. Dev.	Rel. Error
0.22	0.21	0.00458	1.0	0.19	0	3	0	0	22.0
0.61	0.64	0	-2.8	0.61	0	0.2	0	0	61.2
0.80	0.81	0.0308	-1.0	0.80	0.0224	0	0.02	0.0616	79.8
1.09	1.00	0	9.0	0.99	0	10	0.11	0.1025	98.0
2.05	2.00	0	5.3	2.00	0	5.3	1.10	0	95.3
5.04	5.15	0.366	11.5	4.95	0.154	8.5	3.70	0.251	133.5

a. As determined by amperometric titration.

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First, the stability of NCl_3 in aqueous solution with a pH range of 6 to 8 was determined. It was important to know if trichloramine could exist under these conditions and create a possible interference for FAC analysis in drinking water and wastewater. The absorption spectrum of the samples withdrawn at intervals was monitored from 250 to 200 nm to determine trichloramine concentration. The results of this study suggested additional stability experiments using the same procedure at pH 9, 10, and below 6.

The prime objective was to obtain a pure, FAC-free solution of trichloramine; consideration of yield was secondary. Although it was easily prepared in aqueous or non-aqueous solution, a variety of extraction techniques were unsuccessful. Subsequently it was found that trichloramine could be removed from the reaction mixture by a stream of nitrogen gas and could be partially redissolved in distilled chlorine demand-free water. Using this method, trichloramine concentration in the collection bottle increases until the amount of trichloramine being swept out equals the amount introduced by the gas from the reaction mixture. Using the apparatus described previously (Fig. 1), yield was maximized with dilute reaction mixtures and slow flow rates (Table 12). Free chlorine was still present in the collection bottle solution. A low pH was necessary for reaction and the possibility existed that chlorine was being swept out with the trichloramine. In the equilibrium:

$$HCl$$

$$+$$

$$Cl_2 + H_2O \rightleftharpoons HOCl \rightleftharpoons H^+ + OCl^-$$
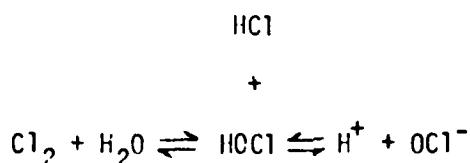
molecular chlorine exists below pH 5.

TABLE 12. SUMMARY OF RESULTS FOR NITROGEN TRICHLORIDE YIELD AT DIFFERENT PRESSURES (SECOND STAGE REGULATOR PRESSURE) OF NITROGEN AS SWEEP GAS

psi	Yield in ppm NCl_3 (mg/L as NCl_2)		% Yield	Time at Maximum (min)
	Theoretical	Actual		
10	143	13.8	9.7	30
15	143	10.9	7.6	25
10	286	24.2	8.5	40
15	286	20.1	7.0	30

It was therefore desirable to find a preparative method for trichlor-
amine that takes place above pH 5. Preparation of trichloramine with
uracil and NaOCl was carried out at pH 7, according to the equation:[13]

$$\text{(uracil)} + HOCl \rightarrow CO_2 + NCl_3 + Cl_3C\text{-}COOH$$
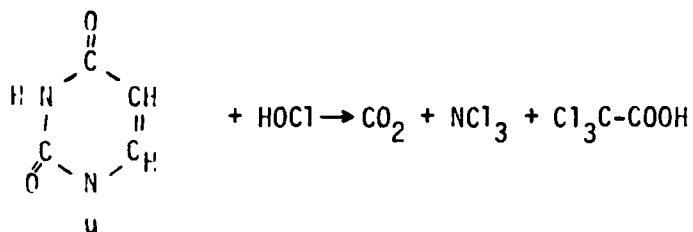
No chlorine (FAC) should be present in the reaction mixture. However,
when the solution resulting from trichloramine in nitrogen being redis-
solved in water was analyzed, chlorine was present. The proportion of
chlorine to trichloramine was roughly equivalent in the two methods of
preparation (Table 13).

TABLE 13. FREE AVAILABLE CHLORINE CONCENTRATIONS IN
DIFFERENT NITROGEN TRICHLORIDE PREPARATIONS

Preparation	NCl_3 (mg/L as NCl_3)	FAC (mg/L as Cl_2)	FAC/NCl_3
I (from NH_4Cl)	14.2	3.5	0.25
	12.9	2.1	0.16
	4.4	0.8	0.18
II (from Uracil)	14.3	3.5	0.24
	9.0	1.7	0.19
	5.0	1.0	0.20

Stability of Trichloramine. Stability studies were first carried out with the reaction mixtures before purging with nitrogen gas to determine how long they could be kept. These studies were performed at a pH of 2 (see Fig. 7). When refrigerated at 6.9°C, 71% of trichloramine remained after 13 days, demonstrating zero-order kinetics; the same solution kept at room temperature followed a first-order rate for decomposition.

To study further the stability of NCl_3 in the pH range 6 to 8, where most water and wastewater analysis is done, additional experiments were performed. Figures 8, 9, and 10 show the decomposition of NCl_3 at pH 6, 7, and 8, respectively. Trichloramine was found to be quite stable at these pH values.

As a result of this determination, decomposition of NCl_3 at pH 9 and 10 was studied (Figs. 11 and 12). The half-life at pH 9 was still greater than 2 hours (Table 14) but dropped drastically to 18 minutes at pH 10, perhaps indicating a change in mechanism. The first 50% of the decomposition at pH 10 follows first-order kinetics while those at pH 6 to 9 do not. Saguinsin[15] found decomposition of trichloramine at pH 9 to be first order with a half-life of only 45 minutes; however, his degradation was carried out in situ. Additional experiments are underway to clarify the results obtained for NCl_3.

Effect of Trichloramine on the DPD, DPD-STEADIFAC Modified, and FACTS Procedures. The final objective was to determine the effect of trichloramine on the DPD, DPD-STEADIFAC Modified, and FACTS test kit procedures. Trichloramine solutions were prepared and four dilutions were made for testing. Although free chlorine could not be eliminated from these solutions, the chlorine content should appear constant for the different tests at a particular concentration if there is no interference by trichloramine. Only three tests were performed for each test at each concentration of trichloramine because of the instability of the trichloramine species. Spectrophotometric measurements of trichloramine were made before and after each series of tests.

The data obtained are summarized in Table 15. The data indicate that the FACTS test procedure produced a higher interference than either the DPD or DPD-STEADIFAC Modified procedures at the two higher levels of nitrogen trichloride, but produced lower interference at lower concentrations of NCl_3. From the data in Table 13, a concentration of free chlorine of 0.96 and 0.6 mg/L as Cl_2 would be expected at nitrogen trichloride levels of 4.80 and 2.97, respectively. Accordingly, all the test procedures recorded an intrusion of NCl_3 as free chlorine at all of the concentrations of NCl_3.

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Figure 7. Decomposition of Aqueous Nitrogen Trichloride at pH 2.
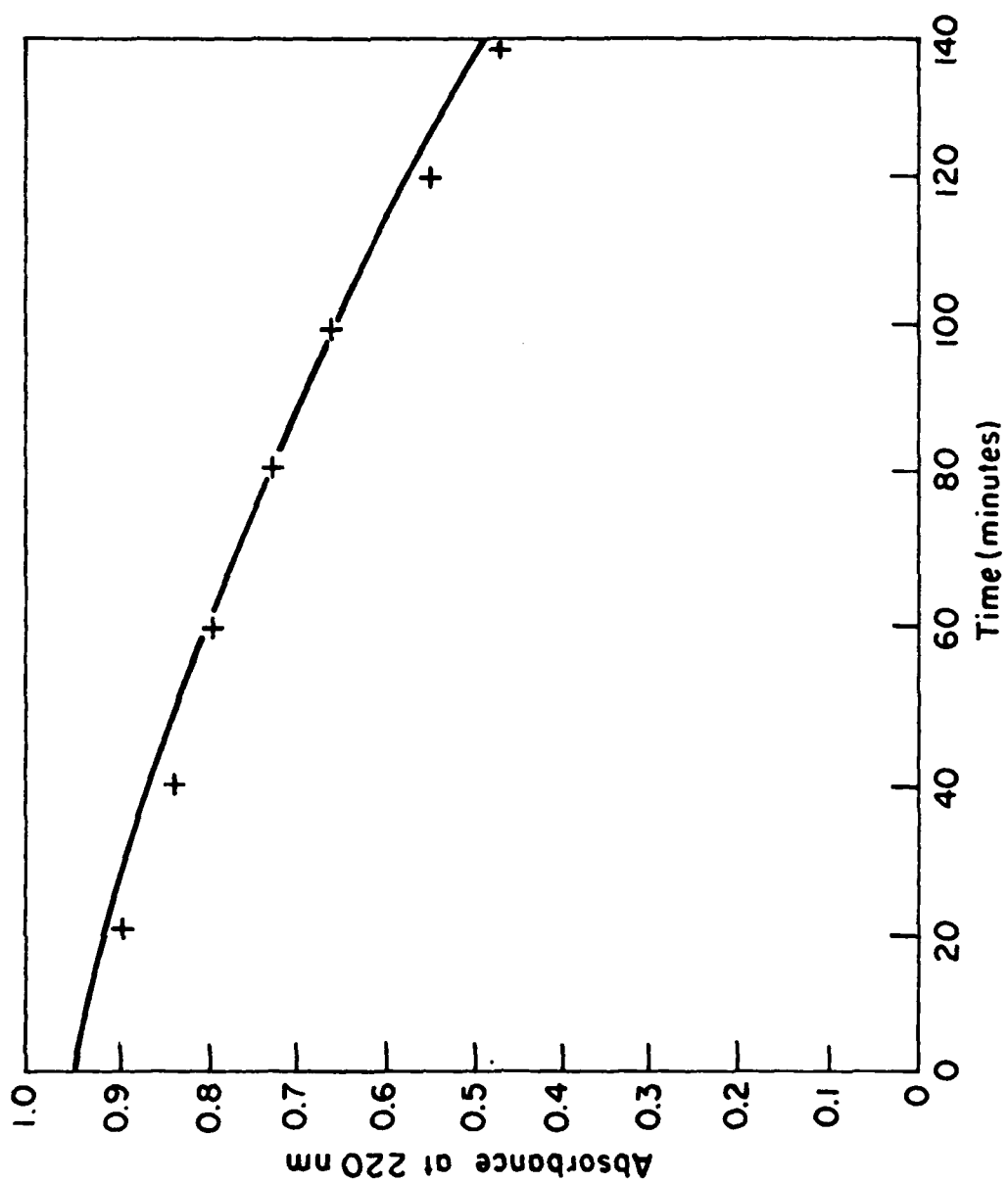
Figure 8. Decomposition of Aqueous Nitrogen Trichloride at pH 6 and 20°C.

37
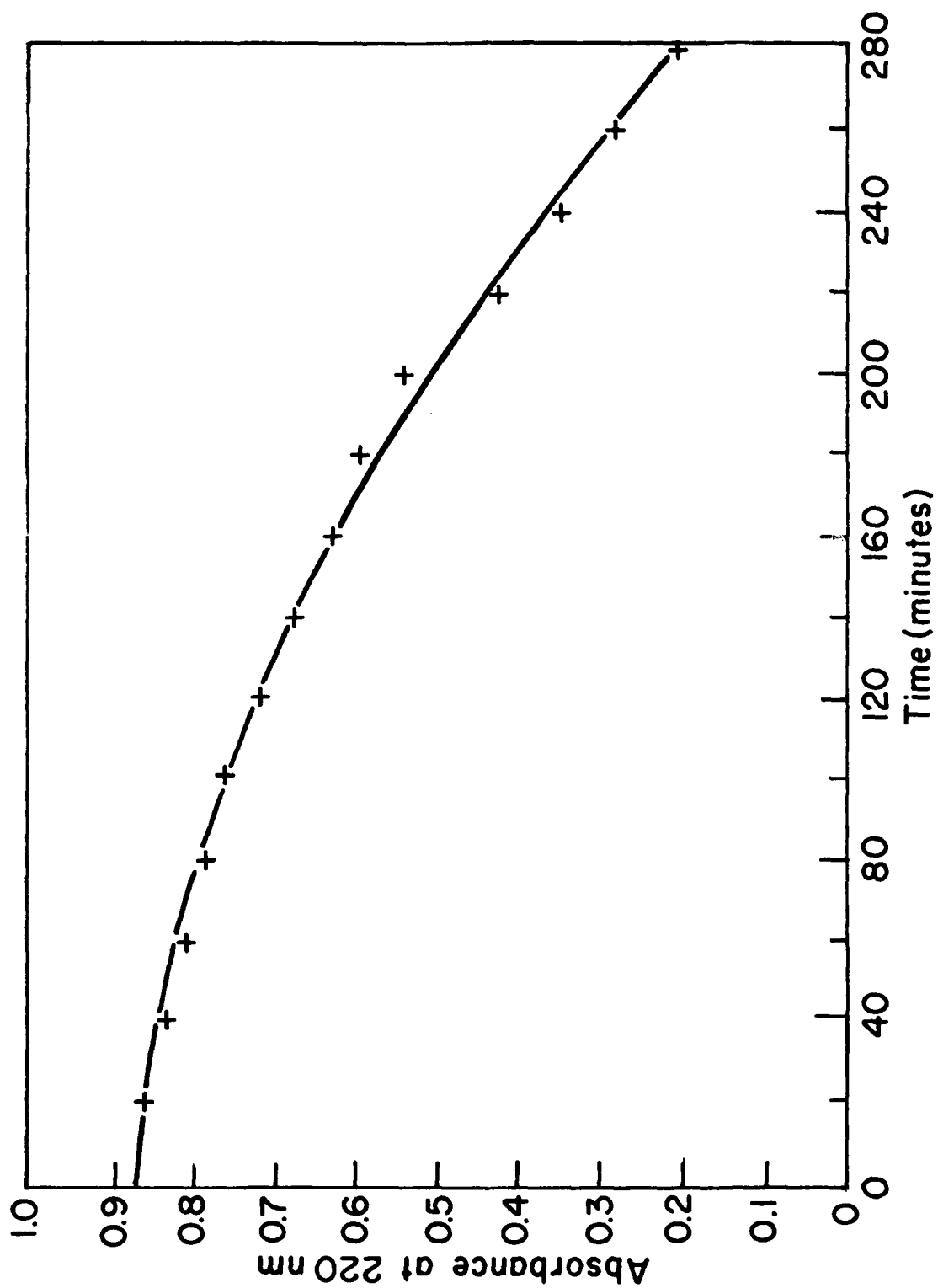
Figure 9. Decomposition of Aqueous Nitrogen Trichloride at pH 7 and 21°C.

38
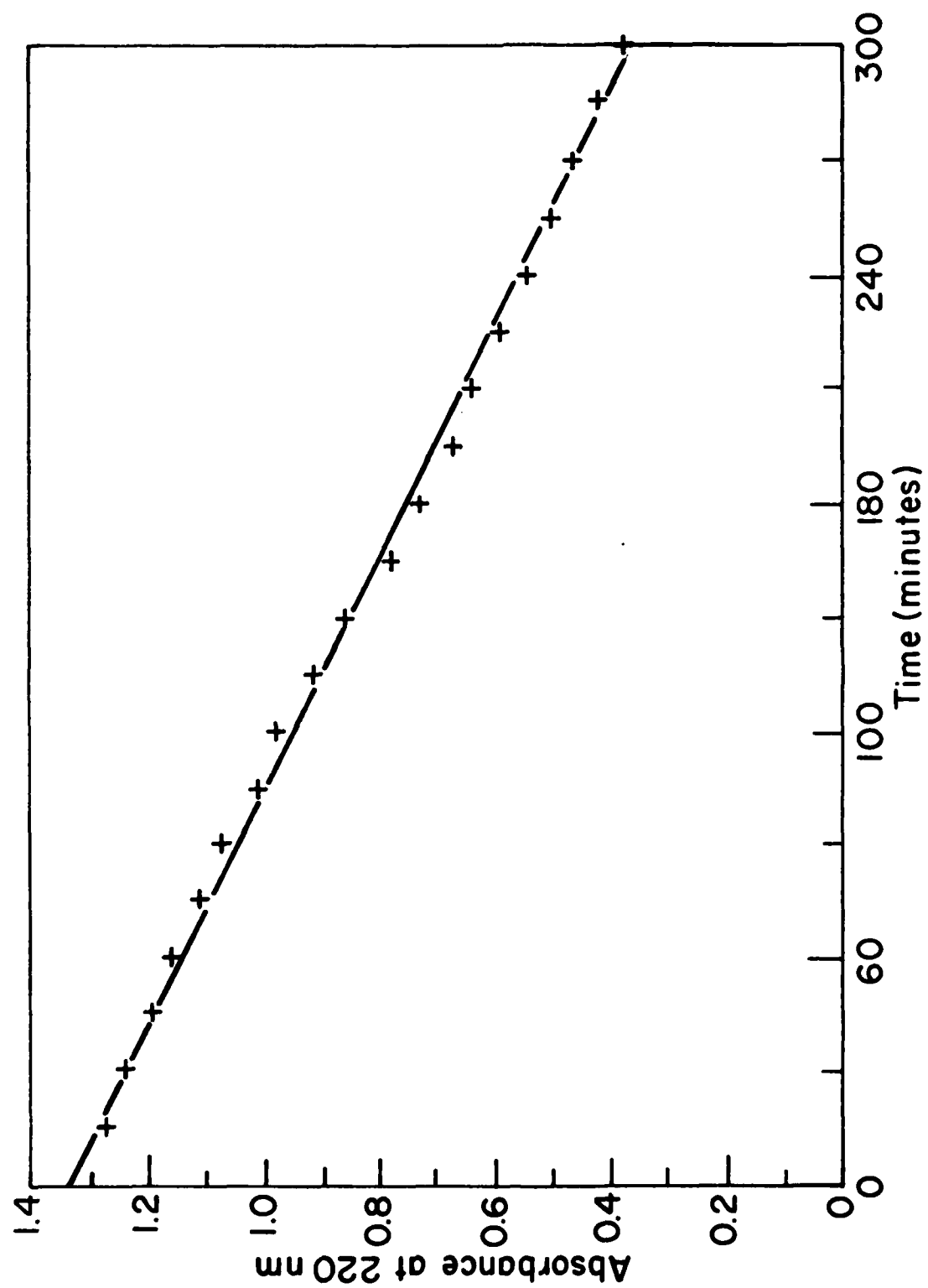
Figure 10. Decomposition of Aqueous Nitrogen Trichloride at pH 8 and 21°C.

39
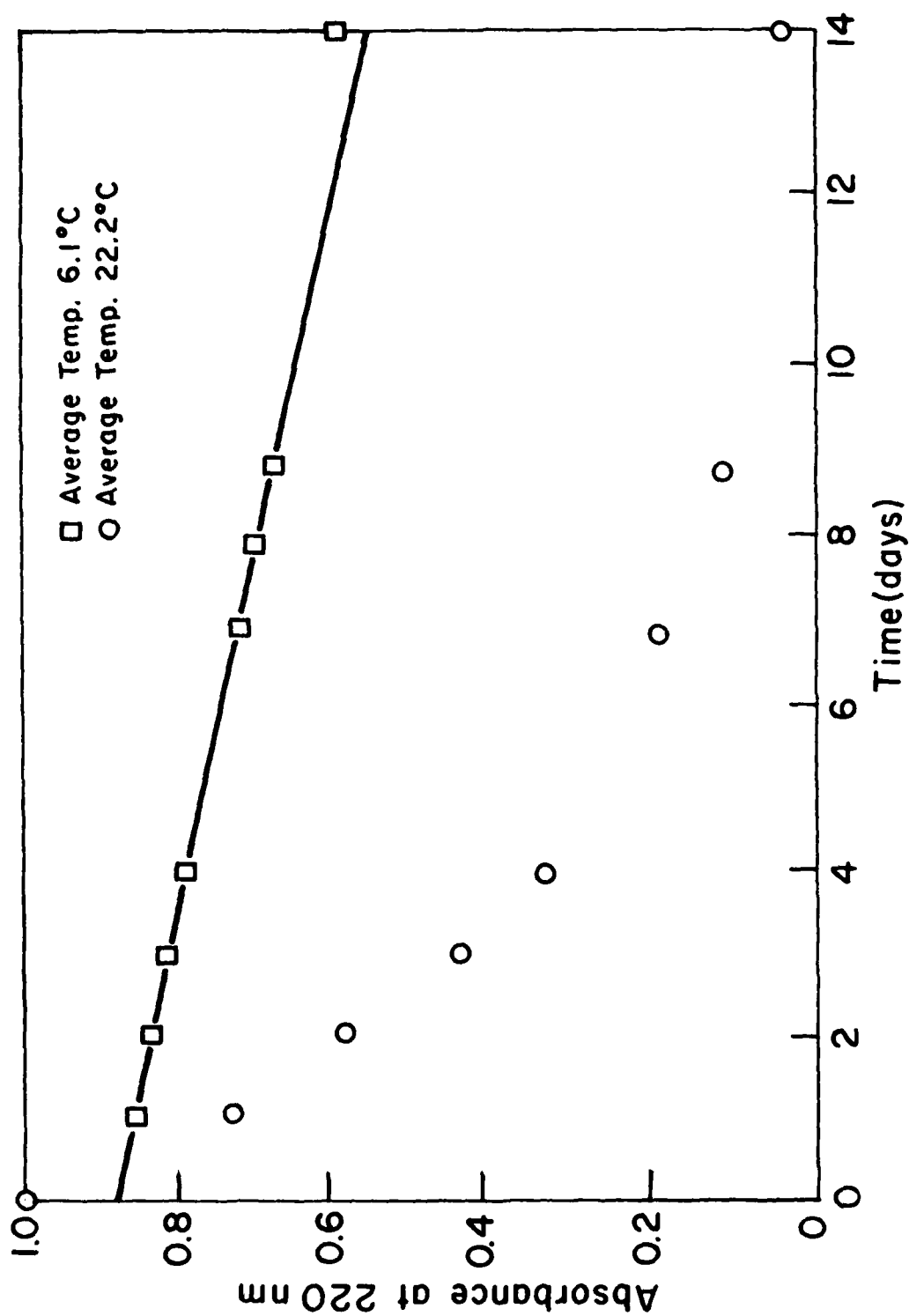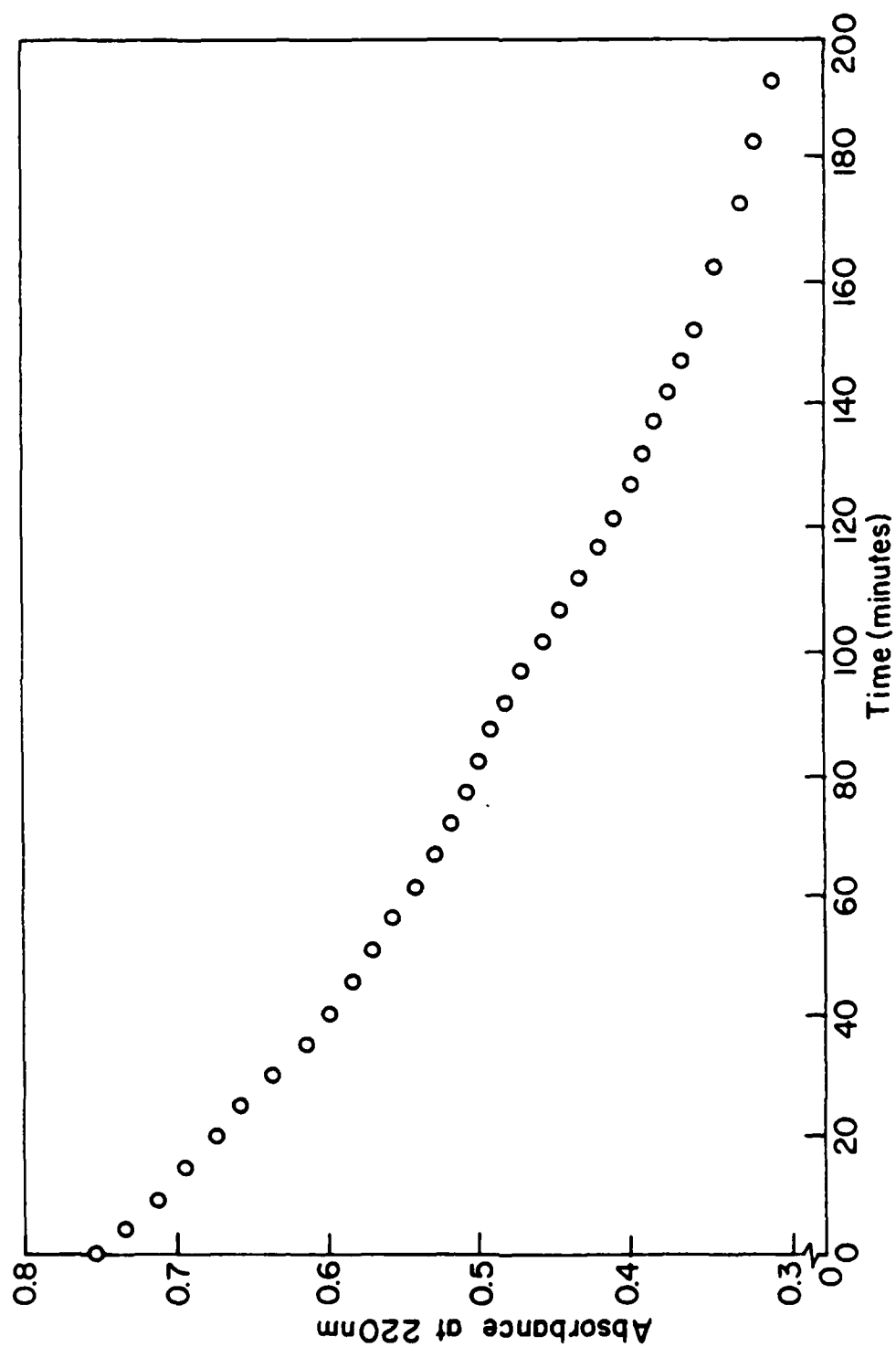
Figure 11. Decomposition of Aqueous Nitrogen Trichloride at pH 9 and 21°C.

40
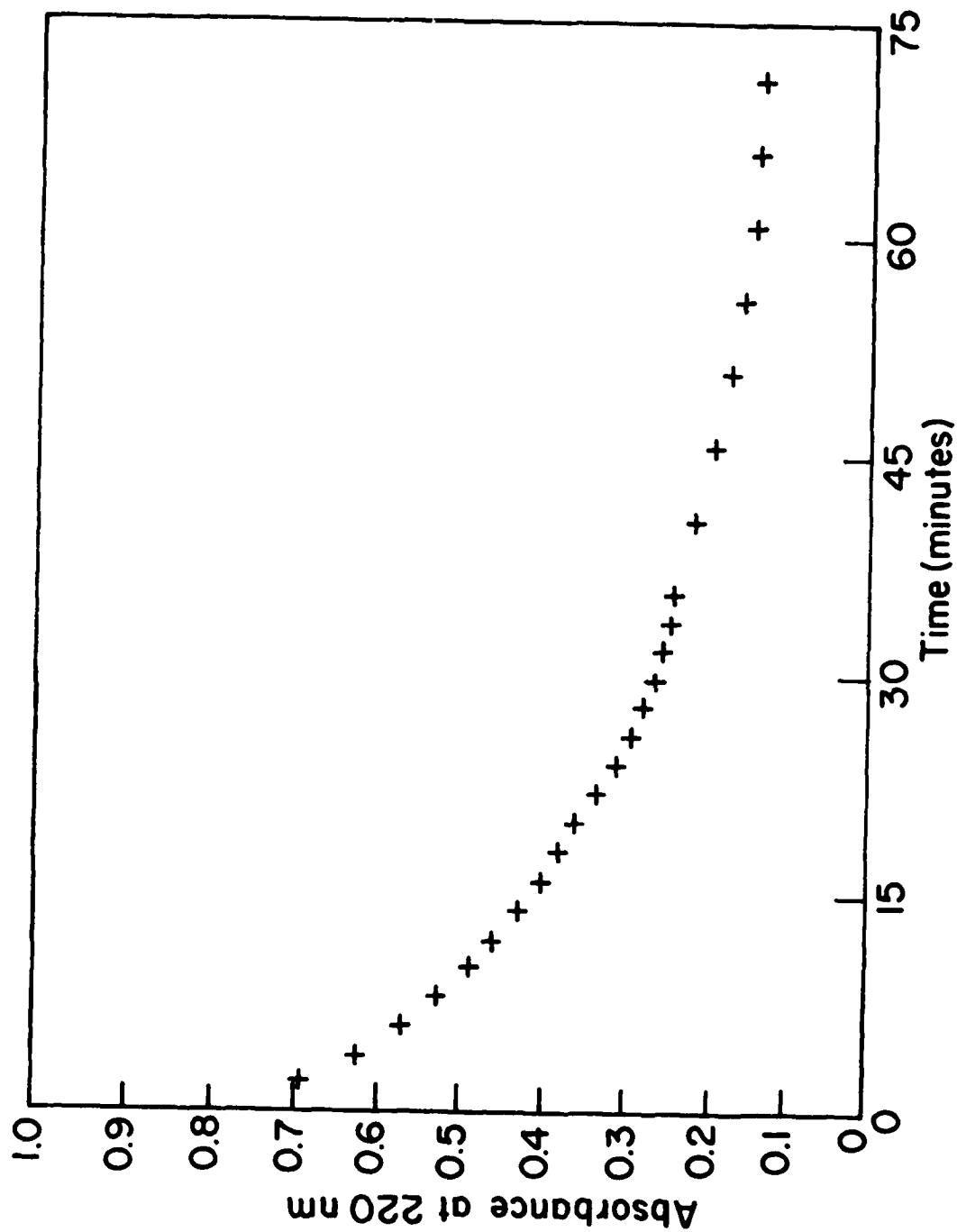
Figure 12. Decomposition of Aqueous Nitrogen Trichloride at pH 10 and 21.2°C.

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TABLE 14. HALF-LIFE OF NITROGEN TRICHLORIDE
SOLUTIONS AT VARIOUS pHs AND TEMPERATURES

pH	Temp (°C)	Half-Life
2	6.1	13 days
2	22.2	2.6 days
6	20.0	136 min
7	21.0	218 min
8	21.0	201 min
9	21.0	140 min
10	21.2	18 min

TABLE 15. FREE AVAILABLE CHLORI E CONCENTRATIONS AS DETERMINED
BY THE DPD, DPD-STEADIFAC MODIFIED, AND FACTS PROCEDURES IN
NITROGEN TRICHLORIDE SOLUTIONS OF VARIOUS CONCENTRATIONS

NCl_3 (mg/L as NCl_3)	FAC (mg/L as Cl_2)		
	DPD	DPD-STEADIFAC Modified	FACTS
4.80	2.59	1.55	4.07
2.97	1.79	1.27	2.54
1.08	0.71	0.58	0.51
0.62	0.35	0.29	0.05

CONCLUSIONS

1. The FACTS test procedure showed no intrusion into the free available chlorine reading from concentrations of monochloramine up to 24 mg/L as Cl_2, 1 minute after mixing the reagents and reading the color. However, after 5 minutes, the two high concentrations of monochloramine, 13.2 and 24 mg/L as Cl_2, did yield an apparent free chlorine reading of approximately 0.2 mg/L as Cl_2.

2. The DPD test procedure produced no apparent free chlorine readings 1 minute after mixing for the two lower levels of monochloramine, 1.2 and 3.5 mg/L as Cl_2. At monochloramine concentrations of 6.4, 13.2, and 24.2, apparent free chlorine levels were 0.2, 0.54, and 1.35, respectively, after 1 minute. When 5 minutes had elapsed between addition of reagent and color reading, all levels of monochloramine 1.2 through 24.2 mg/L as Cl_2 gave apparent free chlorine readings.

3. The average rate of breakthrough from the five levels of monochloramine tested was 4.48 percent/minute 5 minutes after mixing.

4. The FACTS test procedure showed no intrusion into the free available chlorine readings for levels of dichloramine through 20 mg/L as Cl_2.

5. The DPD test procedure showed intrusion into the free available chlorine readings only at the 20 mg/L as Cl_2 dichloramine concentration 5 minutes after mixing reagents.

6. No intrusion into the free available chlorine reading was observed from either mono- or dichloramine for the DPD-STEADIFAC or the DPD-STEADIFAC Modified procedure.

7. The DPD-STEADIFAC procedure as originally published has a limit of detection of 1 mg/L of free available chlorine as Cl_2. Therefore, this is an unacceptable procedure for the determination of low levels of free available chlorine.

8. The DPD-STEADIFAC Modified procedure does not suffer from a level of sensitivity and appears to be more linear through the range 0.2 to 4.0 mg/L free available chlorine as Cl_2.

9. The three DPD procedures all showed greater fading of colored product at lower FAC concentrations than at higher concentrations. In all cases, the fading was substantially higher than for data previously published for the FACTS procedure.

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10. The thioacetamide solutions were tested through a 4.5-month period with no adverse effect observed.

11. The FACTS procedure was shown to have a lower limit of detection of 0.014 mg/L as Cl_2 as compared with 0.021 mg/L as Cl_2 for the DPD procedure.

12. The DPD and DPD-STEADIFAC Modified procedure were shown to have comparable accuracy and precision when measuring free available chlorine in synthetic waters through the range 0.22 to 5.04 mg/L as Cl_2. The DPD-STEADIFAC procedure, although having a comparable precision, had an accuracy much poorer than the other two DPD procedures.

13. All three test procedures--DPD, DPD-STEADIFAC Modified, and FACTS-- showed an intrusion of NCl_3 into the free chlorine reading. The magnitude of the intrusion was shown to be greater for FACTS at the two higher NCl_3 concentrations and greater for the DPD procedure at the two lower NCl_3 concentrations.

BIBLIOGRAPHY

1. Meier, E.P., W.J. Cooper, and C.A. Sorber, "Development of a Rapid Specific Free Available Chlorine Test with Syringaldazine (FACTS)," Technical Report 7405, US Army Medical Bioengineering Research and Development Laboratory, Aberdeen Proving Ground, MD (May 1974) AD 780857.

2. Sorber, C.A., W.J. Cooper, and E.P. Meier, in <u>Disinfection Water and Wastewater</u>, J.D. Johnson, Ed., Chapter 5, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1975).

3. Cooper, W.J., C.A. Sorber, and E.P. Meier, "A Rapid Specific Free Available Chlorine Test with Syringaldazine," <u>J</u>. <u>Amer</u>. <u>Water Works Assoc</u>., 67(1):34 (1975).

4. Guter, K.J., and W.J. Cooper, "The Evaluation of Existing Field Test Kits for Determining Free Chlorine Residuals in Aqueous Solutions," USAMEERU Report 73-03, US Army Medical Environmental Engineering Research Unit, Aberdeen Proving Ground, MD (October 1972) AD 752440.

5. Cooper, W.J., E.P. Meier, J.W. Highfill, and C.A. Sorber, "The Evaluation of Existing Field Test Kits for Determining Free Chlorine Residuals in Aqueous Solutions," Technical Report 7402, US Army Medical Bioengineering Research and Development Laboratory, Aberdeen Proving Ground, MD (April 1974) AD 780054.

6. Guter, K.J., W.J. Cooper, and C.A. Sorber, "Evaluation of Existing Field Test Kits for Determining Free Chlorine Residuals in Aqueous Solutions," <u>J</u>. <u>Amer</u>. <u>Water Works Assoc</u>., 66(1):38 (1974).

7. Palin, A.T., "Notes & Comments," <u>J</u>. <u>Amer</u>. <u>Water Works Assoc</u>., 67(5):206 (April 1975).

8. Palin, A.T., "A New DPD-STEADIFAC Procedure," Presented before the 175th National American Chemical Society Meeting, Division of Environmental Chemistry, Anaheim, CA (March 1978).

9. Palin, A.T., "A New DPD-STEADIFAC Method for the Specific Determination of Free Available Chlorine in the Presence of High Monochloramine," <u>J</u>. <u>Inst</u>. <u>Water Eng</u>. <u>Sci</u>., 32:327 (1978).

10. Meier, E.P., W.J. Cooper, and J.W. Highfill, "Evaluation of the Specificity of the DPD-Glycine and FACTS Test Procedures for Determining Free Available Chlorine," Presented before the 175th National American Chemical Society Meeting, Division of Environmental Chemistry, Anaheim, CA (March 1978).

11. Inorganic Synthesis, William Noyes, (21) p. 65.

12. Chapin, R.M., J. Amer. Chem. Soc., 53(4):912 (1931).

13. Dennis, W.H., Jr., V.P. Olivieri, and C.W. Kruse, "Reaction of Uracil with Hypochlorous Acid," Biochem. Biophys. Res. Comm., 83(1):168 (1978).

14. Standard Methods, 13th Edition, American Public Health Association, New York, NY (1971).

15. Saguinsin, J.L.S.A., "The Chemistry of Aqueous Nitrogen Trichloride," Doctoral Thesis, Harvard University (1974).

APPENDIX A

Data for the Determination of Accuracy and Precision for
Free Available Chlorine Using the DPD, DPD-STEADIFAC, and
DPD-STEADIFAC Modified Procedures in Synthetic Waters

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TABLE A-1. DATA OBTAINED AT FREE AVAILABLE CHLORINE LEVEL OF 0.2

	DPD Procedure Color Comp. 1 min after Mix	DPD-STEADIFAC Color Comp. 1 min after Mix	DPD-STEADIFAC Modified Color Comp. 1 min after Mix
1	0.2	0.0	0.2
2	0.2	0.0	0.2
3	0.2	0.0	0.0[a]
4	0.2	0.0	0.2
5	0.2	0.0	0.2
6	0.2	0.0	0.2
7	0.2	0.0	0.2
8	0.2	0.0	0.2
9	0.2	0.0	0.2
10	0.2	0.0	0.2
11	0.2	0.0	0.2
12	0.2	0.0	0.2
13	0.2	0.0	0.2
14	0.2	0.0	0.2
15	0.3	0.0	0.2
16	0.2	0.0	0.2
17	0.2	0.0	0.2
18	0.2	0.0	0.2
19	0.3	0.0	0.2
20	0.2	0.0	0.2
X	0.21	0.0	0.19
Amperometric titration			
Initial	0.230	0.220	0.210
Final	0.185	0.205	0.190

a. No reaction.

TABLE A-2. DATA OBTAINED AT FREE AVAILABLE CHLORINE LEVEL OF 0.6

	DPD Procedure Color Comp. 1 min after Mix	DPD-STEADIFAC Color Comp. 1 min after Mix	DPD-STEADIFAC Modified Color Comp. 1 min after Mix
1	0.6	0.0	0.6
2	0.7	0.0	0.6
3	0.6	0.0	0.6
4	0.6	0.0	0.6
5	0.6	0.0	0.6
6	0.7	0.0	0.6
7	0.6	0.0	0.6
8	0.7	0.0	0.7
9	0.6	0.0	0.6
10	0.6	0.0	0.7
11	0.6	0.0	0.6
12	0.7	0.0	0.6
13	0.7	0.0	0.6
14	0.6	0.0	0.6
15	0.6	0.0	0.6
16	0.6	0.0	0.6
17	0.7	0.0	0.6
18	0.7	0.0	0.6
19	0.6	0.0	0.6
20	0.7	0.0	0.6
$\bar{X}$	0.64	0.0	0.61

Amperometric titration

Initial	0.605	0.610	0.620
Final	0.595	0.605	0.605

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TABLE A-3. DATA OBTAINED AT FREE AVAILABLE CHLORINE LEVEL OF 1.0

	DPD Procedure Color Comp. 1 min after Mix	DPD-STEADIFAC Color Comp. 1 min after Mix	DPD-STEADIFAC Modified Color Comp. 1 min after Mix
1	1.0	0.2	1.0
2	1.0	0.0	0.9
3	1.0	0.0	1.0
4	1.0	0.2	1.0
5	1.0	0.3	1.0
6	1.0	0.2	1.0
7	1.0	0.0[a]	1.0
8	1.0	0.0	1.0
9	1.0	0.0[a]	0.9
10	1.0	0.3	1.0
11	1.0	0.3	1.0
12	1.0	0.0	1.0
13	1.0	0.2	1.0
14	1.0	0.0[a]	1.0
15	1.0	0.0	1.0
16	1.0	0.2	1.0
17	1.0	0.2	1.0
18	1.0	0.0	1.0
19	1.0	0.0	1.0
20	1.0	0.0	1.0
X	1.0	0.11	0.99

Amperometric titration

Initial	1.050	1.100	1.140
Final	1.000	1.040	1.060

a. No reaction.

TABLE A-4. DATA OBTAINED AT FREE AVAILABLE CHLORINE LEVEL OF 2.0

	DPD Procedure Color Comp. 1 min after Mix	DPD-STEADIFAC Color Comp. 1 min after Mix	DPD-STEADIFAC Modified Color Comp. 1 min after Mix
1	2.0	1.0	2.0
2	2.0	1.25	2.0
3	2.0	1.0	2.0
4	2.0	1.25	2.0
5	2.0	1.0	2.0
6	2.0	1.0	2.0
7	2.0	1.0	2.0
8	2.0	1.25	2.0
9	2.0	1.25	2.0
10	2.0	1.0	2.0
11	2.0	1.25	2.0
12	2.0	1.0	2.0
13	2.0	1.25	2.0
14	2.0	1.0	2.0
15	2.0	1.0	2.0
16	2.0	1.0	2.0
17	2.0	1.25	2.0
18	2.0	1.0	2.0
19	2.0	1.0	2.0
20	2.0	1.25	2.0
X	2.0	1.10	2.0

Amperometric titration

Initial	2.070	2.030	2.060

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