

## Standard Methods for the Examination of Water and Wastewater

### 4500-ClO<sub>2</sub> CHLORINE DIOXIDE\*#(1)

#### 4500-ClO<sub>2</sub> A. Introduction

Because the physical and chemical properties of chlorine dioxide resemble those of chlorine in many respects, read the entire discussion of Residual Chlorine (Section 4500-Cl) before attempting a chlorine dioxide determination.

#### 1. Occurrence and Significance

Chlorine dioxide, ClO<sub>2</sub>, has been used widely as a bleaching agent in the paper and pulp industry. It has been applied to water supplies to combat tastes and odors due to phenolic-type wastes, actinomycetes, and algae, as well as to oxidize soluble iron and manganese to a more easily removable form. It is a disinfectant, and some results suggest that it may be stronger than free chlorine or hypochlorite.

Chlorine dioxide is a deep yellow, volatile, unpleasant-smelling gas that is toxic and under certain conditions may react explosively. It should be handled with care in a vented area. The use of odor to warn of exposure to concentrations of health significance may not be adequate.

There are several methods of generating ClO<sub>2</sub>; for laboratory purposes the acidification of a solution of sodium chlorite followed by suitable scrubbing and capture of the released gaseous ClO<sub>2</sub> is the most practical. CAUTION: *Sodium chlorite is a powerful oxidizer; keep out of direct contact with oxidizable material to avoid possibility of explosion.*

#### 2. Selection of Method

The iodometric method (B) gives a very precise measure of total available strength of a solution in terms of its ability to liberate iodine from iodide. However, ClO<sub>2</sub>, chlorine, chlorite, and hypochlorite are not distinguished easily by this technique. It is designed primarily, and best used, for standardizing ClO<sub>2</sub> solutions needed for preparation of temporary standards. It often is inapplicable to industrial wastes.

The amperometric methods (C and E) are useful when a knowledge of the various chlorine fractions in a water sample is desired. They distinguish various chlorine compounds of interest with good accuracy and precision, but require specialized equipment and considerable analytical skill.

The *N,N*-diethyl-*p*-phenylenediamine (DPD) method (D) has the advantages of a relatively easy-to-perform colorimetric test with the ability to distinguish between ClO<sub>2</sub> and some forms of chlorine. This technique is not as accurate as the amperometric method, but should yield results adequate for many common applications. NOTE: Reports in the literature indicate that the DPD method is subject to interference from monochloramine and chloraminoacetic acid, and the chlorite anion.<sup>1</sup>

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### 3. Sampling and Storage

Determine  $\text{ClO}_2$  promptly after collecting the sample. Do not expose sample to sunlight or strong artificial light and do not aerate to mix. Most of these methods can be performed on site, with prior calibration in the laboratory. Minimum  $\text{ClO}_2$  losses occur when the determination is completed immediately at the site of sample collection.

### 4. Reference

1. CHISWELL, B. & K.R. O'HALLORAN. 1991. Use of Lissamine Green B as a spectrophotometric reagent for the determination of low residuals of chlorine dioxide. *Analyst* 116:657.

### 5. Bibliography

- INGOLS, R.S. & G.M. RIDENOUR. 1948. Chemical properties of chlorine dioxide in water treatment. *J. Amer. Water Works Assoc.* 40:1207.
- PALIN, A.T. 1948. Chlorine dioxide in water treatment. *J. Inst. Water Eng.* 11:61.
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- FEUSS, J.V. 1964. Problems in determination of chlorine dioxide residuals. *J. Amer. Water Works Assoc.* 56:607.
- MASSCHELEIN, W. 1966. Spectrophotometric determination of chlorine dioxide with acid chrome violet K. *Anal. Chem.* 38:1839.
- MASSCHELEIN, W. 1969. Les Oxydes de Chlore et le Chlorite de Sodium. Dunod, Paris, Chapter XI.

## 4500- $\text{ClO}_2$ B. Iodometric Method

### 1. General Discussion

*a. Principle:* A pure solution of  $\text{ClO}_2$  is prepared from gaseous  $\text{ClO}_2$  by slowly adding dilute  $\text{H}_2\text{SO}_4$  to a sodium chlorite ( $\text{NaClO}_2$ ) solution. Contaminants such as chlorine are removed from the gas stream by a  $\text{NaClO}_2$  scrubber; the gas is passed into distilled water in a steady stream of air. See CAUTION, ¶ A.1.

$\text{ClO}_2$  releases free iodine from a KI solution acidified with acetic acid or  $\text{H}_2\text{SO}_4$ . The liberated iodine is titrated with a standard solution of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), with starch as the indicator.

*b. Interference:* There is little interference in this method, but temperature and strong light affect solution stability. Minimize  $\text{ClO}_2$  losses by storing stock  $\text{ClO}_2$  solution in a dark refrigerator and by preparing and titrating dilute  $\text{ClO}_2$  solutions for standardization purposes at the lowest practicable temperature and in subdued light.

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*c. Minimum detectable concentration:* One drop (0.05 mL) of 0.01*N* (0.01*M*)  $\text{Na}_2\text{S}_2\text{O}_3$  is equivalent to 20  $\mu\text{g ClO}_2/\text{L}$  (or 40  $\mu\text{g/L}$  in terms of available chlorine) when a 500-mL sample is titrated.

### 2. Reagents

All reagents listed for the determination of residual chlorine in Section 4500-Cl.B.2*a* - Section 4500-Cl.B.2*g* are required. Also needed are the following:

*a. Stock chlorine dioxide solution:* Prepare a gas generating and absorbing system as illustrated in Figure 4500-ClO<sub>2</sub>:1. Connect aspirator flask, 500-mL capacity, with rubber tubing to a source of purified compressed air. Let air bubble through a layer of 300 mL distilled water in flask and then pass through a glass tube ending within 5 mm of the bottom of the 1-L gas-generating bottle. Conduct evolved gas via glass tubing through a scrubber bottle containing saturated  $\text{NaClO}_2$  solution or a tower packed with flaked  $\text{NaClO}_2$ , and finally, via glass tubing, into a 2-L borosilicate glass collecting bottle where the gas is absorbed in 1500 mL distilled water. Provide an air outlet tube on collecting bottle for escape of air. Select for gas generation a bottle constructed of strong borosilicate glass and having a mouth wide enough to permit insertion of three separate glass tubes: the first leading almost to the bottom for admitting air, the second reaching below the liquid surface for gradual introduction of  $\text{H}_2\text{SO}_4$ , and the third near the top for exit of evolved gas and air. Fit to second tube a graduated cylindrical separatory funnel to contain  $\text{H}_2\text{SO}_4$ . Locate this system in a fume hood with an adequate shield.

Dissolve 10 g  $\text{NaClO}_2$  in 750 mL distilled water and place in generating bottle. Carefully add 2 mL conc  $\text{H}_2\text{SO}_4$  to 18 mL distilled water and mix. Transfer to funnel. Connect flask to generating bottle, generating bottle to scrubber, and the latter to collecting bottle. Pass a smooth current of air through the system, as evidenced by the bubbling rate in all bottles.

Introduce 5-mL increments of  $\text{H}_2\text{SO}_4$  from funnel into generating bottle at 5-min intervals. Continue air flow for 30 min after last portion of acid has been added.

Store yellow stock solution in glass-stoppered dark-colored bottle in a dark refrigerator. The concentration of  $\text{ClO}_2$  thus prepared varies between 250 and 600 mg/L, corresponding to approximately 500 to 1200 mg free chlorine/L.

*b. Standard chlorine dioxide solution:* Use this solution for preparing temporary  $\text{ClO}_2$  standards. Dilute required volume of stock  $\text{ClO}_2$  solution to desired strength with chlorine-demand-free water (see Section 4500-Cl.C.3*m*). Standardize solution by titrating with standard 0.01*N* (0.01*M*) or 0.025*N* (0.025*M*)  $\text{Na}_2\text{S}_2\text{O}_3$  titrant in the presence of KI, acid, and starch indicator by following the procedure given in ¶ 3 below. A full or nearly full bottle of chlorine or  $\text{ClO}_2$  solution retains its titer longer than a partially full one. When repeated withdrawals reduce volume to a critical level, standardize diluted solution at the beginning, midway in the series of withdrawals, and at the end of the series. Shake contents thoroughly before drawing off needed solution from middle of the glass-stoppered dark-colored bottle. Prepare this solution frequently.

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### 3. Procedure

Select volume of sample, prepare for titration, and titrate sample and blank as described in Section 4500-Cl.B.3. The only exception is the following: *Let ClO<sub>2</sub> react in the dark with acid and KI for 5 min before starting titration.*

### 4. Calculations

Express ClO<sub>2</sub> concentrations in terms of ClO<sub>2</sub> or as free chlorine content. Free chlorine is defined as the total oxidizing power of ClO<sub>2</sub> measured by titrating iodine released by ClO<sub>2</sub> from an acidic solution of KI. Calculate result in terms of chlorine itself.

For standardizing ClO<sub>2</sub> solution:

$$\text{mg ClO}_2/\text{mL} = \frac{(A \pm B) \times N \times 13.49}{\text{mL sample titrated}}$$

For determining ClO<sub>2</sub> temporary standards:

$$\text{mg ClO}_2 \text{ as Cl}_2/\text{mL} = \frac{(A \pm B) \times N \times 35.45}{\text{mL sample titrated}}$$

where:

*A* = mL titration for sample,

*B* = mL titration for blank (positive or negative, see Section 4500-Cl.B.3*d*), and

*N* = normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> = molarity of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

### 5. Bibliography

POST, M.A. & W.A. MOORE. 1959. Determination of chlorine dioxide in treated surface waters. *Anal. Chem.* 31:1872.

## 4500-ClO<sub>2</sub> C. Amperometric Method I

### 1. General Discussion

*a. Principle:* The amperometric titration of ClO<sub>2</sub> is an extension of the amperometric method for chlorine. By performing four titrations with phenylarsine oxide, free chlorine (including hypochlorite and hypochlorous acid), chloramines, chlorite, and ClO<sub>2</sub> may be determined separately. The first titration step consists of conversion of ClO<sub>2</sub> to chlorite and chlorate through addition of sufficient NaOH to produce a pH of 12, followed by neutralization to a pH of 7 and titration of free chlorine. In the second titration KI is added to a sample that has been treated similarly with alkali and had the pH readjusted to 7; titration

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yields free chlorine and monochloramine. The third titration involves addition of KI and pH adjustment to 7, followed by titration of free chlorine, monochloramine, and one-fifth of the available  $\text{ClO}_2$ . In the fourth titration, addition of sufficient  $\text{H}_2\text{SO}_4$  to lower the pH to 2 enables all available  $\text{ClO}_2$  and chlorite, as well as the total free chlorine, to liberate an equivalent amount of iodine from the added KI and thus be titrated.

*b. Interference:* The interferences described in Section 4500-Cl.D.1*b* apply also to determination of  $\text{ClO}_2$ .

### 2. Apparatus

The apparatus required is given in Section 4500-Cl.D.2*a* through *d*.

### 3. Reagents

All reagents listed for the determination of chlorine in Section 4500-Cl.D.3 are required. Also needed are the following:

- a. Sodium hydroxide, NaOH, 6N (6M).*
- b. Sulfuric acid,  $\text{H}_2\text{SO}_4$ , 6N (3M), 1 + 5.*

### 4. Procedure

Minimize effects of pH, time, and temperature of reaction by standardizing all conditions.

*a. Titration of free available chlorine (hypochlorite and hypochlorous acid):* Add sufficient 6N (6M) NaOH to raise sample pH to 12. After 10 min, add 6N (3M)  $\text{H}_2\text{SO}_4$  to lower pH to 7. Titrate with standard phenylarsine oxide titrant to the amperometric end point as given in Section 4500-Cl.D. Record result as *A*.

*b. Titration of free available chlorine and chloramine:* Add 6N (6M) NaOH to raise sample pH to 12. After 10 min, add 6N (3M)  $\text{H}_2\text{SO}_4$  to reduce pH to 7. Add 1 mL KI solution. Titrate with standard phenylarsine oxide titrant to the amperometric end point. Record result as *B*.

*c. Titration of free available chlorine, chloramine, and one-fifth of available  $\text{ClO}_2$ :* Adjust sample pH to 7 with pH 7 phosphate buffer solution. Add 1 mL KI solution. Titrate with standard phenylarsine oxide titrant to the amperometric end point. Record result as *C*.

*d. Titration of free available chlorine, chloramines,  $\text{ClO}_2$ , and chlorite:* Add 1 mL KI solution to sample. Add sufficient 6N (3M)  $\text{H}_2\text{SO}_4$  to lower pH to 2. After 10 min, add sufficient 6N (6M) NaOH to raise pH to 7. Titrate with standard phenylarsine oxide titrant to the amperometric end point. Record result as *D*.

### 5. Calculation

Convert individual titrations (*A*, *B*, *C*, and *D*) into chlorine concentration by the following equation:

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$$\text{mg Cl as Cl}_2/\text{L} = \frac{E \times 200}{\text{mL sample}}$$

where:

$E$  = mL phenylarsine oxide titration for each individual sample  $A$ ,  $B$ ,  $C$ , or  $D$ .

Calculate  $\text{ClO}_2$  and individual chlorine fractions as follows:

$$\begin{aligned} \text{mg ClO}_2 \text{ as ClO}_2/\text{L} &= 1.9 (C - B) \\ \text{mg ClO}_2 \text{ as Cl}_2/\text{L} &= 5 (C - B) \\ \text{mg free available chlorine/L} &= A \\ \text{mg chloramine/L as chlorine} &= B - A \\ \text{mg chlorite/L as chlorine} &= 4B - 5C + D \end{aligned}$$

## 6. Bibliography

HALLER, J.F. & S.S. LISTEK. 1948. Determination of chlorine dioxide and other active chlorine compounds in water. *Anal. Chem.* 20:639.

### 4500- $\text{ClO}_2$ D. DPD Method

#### 1. General Discussion

*a. Principle:* This method is an extension of the *N,N*-diethyl-*p*-phenylenediamine (DPD) method for determining free chlorine and chloramines in water.  $\text{ClO}_2$  appears in the first step of this procedure but only to the extent of one-fifth of its total available chlorine content corresponding to reduction of  $\text{ClO}_2$  to chlorite ion. If the sample is then acidified in the presence of iodide the chlorite also reacts. When neutralized by subsequent addition of bicarbonate, the color thus produced corresponds to the total available chlorine content of the  $\text{ClO}_2$ . If chlorite is present in the sample, this will be included in the step involving acidification and neutralization. Chlorite that did not result from  $\text{ClO}_2$  reduction by the procedure will cause a positive error equal to twice this chlorite concentration. In evaluating mixtures of these various chloro-compounds, it is necessary to suppress free chlorine by adding glycine before reacting the sample with DPD reagent. Differentiation is based on the fact that glycine converts free chlorine instantaneously into chloroaminoacetic acid but has no effect on  $\text{ClO}_2$ .

*b. Interference:* The interference by oxidized manganese described in Section 4500-Cl.F.1d applies also to  $\text{ClO}_2$  determination. Manganese interference appears as an increase in the first titrations after addition of DPD, with or without KI, and irrespective of whether there has been prior addition of glycine. Titration readings must be corrected

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suitably. Interference by chromate in wastewaters may be corrected similarly.

Iron contributed to the sample by adding ferrous ammonium sulfate (FAS) titrant may activate chlorite so as to interfere with the first end point of the titration. Suppress this effect with additional EDTA, disodium salt.

Exercise caution in the selection of this method, because of interferences from monochloramine and chloraminoacetic acid and the chlorite anion.

### 2. Reagents

Reagents required in addition to those for the DPD free-combined chlorine method as listed in Section 4500-Cl.F.2 are as follows:

- a. *Glycine solution*: Dissolve 10 g  $\text{NH}_2\text{CH}_2\text{COOH}$  in 100 mL distilled water.
- b. *Sulfuric acid solution*: Dilute 5 mL conc  $\text{H}_2\text{SO}_4$  to 100 mL with distilled water.
- c. *Sodium bicarbonate solution*: Dissolve 27.5 g  $\text{NaHCO}_3$  in 500 mL distilled water.
- d. *EDTA*: Disodium salt of ethylenediamine tetraacetic acid, solid.

### 3. Procedure

For samples containing more than 5 mg/L total available chlorine follow the dilution procedure given in Section 4500-Cl.F.3.

a. *Chlorine dioxide*: Add 2 mL glycine solution to 100 mL sample and mix. Place 5 mL each of buffer reagent and DPD indicator solution in a separate titration flask and mix (or use about 500 mg DPD powder). Add about 200 mg EDTA, disodium salt. Then add glycine-treated sample and mix. Titrate rapidly with standard FAS titrant until red color is discharged (Reading *G*).

b. *Free available chlorine and chloramine*: Using a second 100-mL sample follow the procedures of Section 4500-Cl.F.3a adding about 200 mg EDTA, disodium salt, initially with the DPD reagents (Readings *A*, *B*, and *C*).

c. *Total available chlorine including chlorite*: After obtaining Reading *C* add 1 mL  $\text{H}_2\text{SO}_4$  solution to the same sample in titration flask, mix, and let stand about 2 min. Add 5 mL  $\text{NaHCO}_3$  solution, mix, and titrate (Reading *D*).

d. *Colorimetric procedure*: Instead of titration with standard FAS solution, colorimetric procedures may be used to obtain the readings at each stage. Calibrate colorimeters with standard permanganate solution as directed in Section 4500-Cl.G.4a. Use of additional EDTA, disodium salt, with the DPD reagents is not required in colorimetric procedures.

### 4. Calculations

For 100 mL sample, 1 mL FAS solution = 1 mg available chlorine/L.

*In the absence of chlorite:*

$$\text{Chlorine dioxide} = 5G \text{ (or } 1.9G \text{ expressed as } \text{ClO}_2\text{)}$$

$$\text{Free available chlorine} = A - G$$

$$\text{Monochloramine} = B - A$$

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$$\begin{aligned}\text{Dichloramine} &= C - B \\ \text{Total available chlorine} &= C + 4G\end{aligned}$$

If the step leading to Reading *B* is omitted, monochloramine and dichloramine are obtained together when:

$$\text{Combined available chlorine} = C - A$$

If it is desired to check for presence of chlorite in sample, obtain Reading *D*. Chlorite is indicated if *D* is greater than  $C + 4G$ .

*In the presence of chlorite:*

$$\begin{aligned}\text{Chlorine dioxide} &= 5G \text{ (or } 1.9G \text{ expressed as } \text{ClO}_2\text{)} \\ \text{Chlorite} &= D - (C + 4G) \\ \text{Free available chlorine} &= A - G \\ \text{Monochloramine} &= B - A \\ \text{Dichloramine} &= C - B \\ \text{Total available chlorine} &= D\end{aligned}$$

If *B* is omitted,

$$\text{Combined available chlorine} = C - A$$

### 5. Bibliography

- PALIN, A.T. 1960. Colorimetric determination of chlorine dioxide in water. *Water Sewage Works* 107:457.
- PALIN, A.T. 1967. Methods for the determination, in water, of free and combined available chlorine, chlorine dioxide and chlorite, bromine, iodine, and ozone using diethyl-p-phenylenediamine (DPD). *J. Inst. Water Eng.* 21:537.
- PALIN, A.T. 1974. Analytical control of water disinfection with special reference to differential DPD methods for chlorine, chlorine dioxide, bromine, iodine and ozone. *J. Inst. Water Eng.* 28:139.
- PALIN, A.T. 1975. Current DPD methods for residual halogen compounds and ozone in water. *J. Amer. Water Works Assoc.* 67:32.

### 4500-ClO<sub>2</sub> E. Amperometric Method II

#### 1. General Discussion

*a. Principle:* Like Amperometric Method I (Section 4500-ClO<sub>2</sub>.C), this procedure entails successive titrations of combinations of chlorine species. Subsequent calculations determine the concentration of each species. The equilibrium for reduction of the chlorine species of interest by iodide is pH-dependent.

The analysis of a sample for chlorine, chlorine dioxide, chlorite, and chlorate requires the

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following steps: determination of all of the chlorine (free plus combined) and one-fifth of the chlorine dioxide at pH 7; lowering sample pH to 2 and determination of the remaining four-fifths of the  $\text{ClO}_2$  and all of the chlorite (the chlorite measured in this step comes from the chlorite originally present in the sample and that formed in the first titration); preparation of a second sample by purging with nitrogen to remove  $\text{ClO}_2$  and by reacting with iodide at pH 7 to remove any chlorine remaining; lowering latter sample pH to 2 and determination of all chlorite present (this chlorite only comes from the chlorite originally present in the sample); and, in a third sample, determination of all of the relevant, oxidized chlorine species—chlorine, chlorine dioxide, chlorite, and chlorate—after reduction in hydrochloric acid.<sup>1</sup>

This procedure can be applied to concentrated solutions (10 to 100 mg/L) or dilute solutions (0.1 to 10 mg/L) by appropriate selection of titrant concentration and sample size.

*b. Interferences:* At pH values above 4, significant iodate formation is possible if iodine is formed in the absence of iodide;<sup>2</sup> this results in a negative bias in titrating the first and second samples. Acidification of these samples causes reduction of iodate to iodine and a positive bias. To prevent formation of iodate add 1 g KI granules to stirred sample.

A positive bias results from oxidation of iodide to iodine by dissolved oxygen in strongly acidic solutions.<sup>1</sup> To minimize this bias, use bromide as the reducing agent in titrating the third sample (bromide is not oxidized by oxygen under these conditions). After reaction is completed, add iodide, which will be oxidized to iodine by the bromine formed from the reduction of the original chlorine species. Add iodide carefully so that bromine gas is not lost. Rapid dilution of the sample with sodium phosphate decreases sample acidity and minimizes oxidation of iodide by oxygen. The pH of the solution to be titrated should be between 1.0 and 2.0. Carry a blank through the procedure as a check on iodide oxidation.

The potential for interferences from manganese, copper, and nitrate is minimized by buffering the sample to  $\text{pH} \geq 4$ .<sup>3,4</sup> For the method presented here, the low pH required for the chlorite and chlorate analyses provides conditions favorable to manganese, copper, and nitrite interferences.

### 2. Apparatus

*a. Titrators:* See Section 4500-Cl.D.2a through *d*. Amperometric titrators with a platinum-platinum electrode system are more stable and require less maintenance. (NOTE: Chlorine dioxide may attack adhesives used to connect the platinum plate to the electrode, resulting in poor readings.)

If a potentiometric titrator is used, provide a platinum sensing electrode and a silver chloride reference electrode for end-point detection.

*b. Glassware:* Store glassware used in this method separately from other laboratory glassware and do not use for other purposes because  $\text{ClO}_2$  reacts with glass to form a hydrophobic surface coating. To satisfy any  $\text{ClO}_2$  demand, before first use immerse all glassware in a strong  $\text{ClO}_2$  solution (200 to 500 mg/L) for 24 h and rinse only with water between uses.

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*c. Sampling:*  $\text{ClO}_2$  is volatile and will vaporize easily from aqueous solution. When sampling a liquid stream, minimize contact with air by placing a flexible sample line to reach the bottom of the sample container, letting several container volumes overflow, slowly removing sample line, and capping container with minimum headspace. Protect from sunlight. Remove sample portions with a volumetric pipet with pipet tip placed at bottom of container. Drain pipet by placing its tip below the surface of reagent or dilution water.

### 3. Reagents

- a. Standard sodium thiosulfate, 0.100N (0.100M):* See Section 4500-Cl.B.2c.
- b. Standard phenylarsine oxide, 0.005 64N (0.005 64M):* See Section 4500-Cl.C.3a. (Weigh out 1.25 g phenylarsine oxide and standardize to 0.005 64M.)
- c. Phosphate buffer solution, pH 7:* See Section 4500-Cl.D.3b.
- d. Potassium iodide, KI, granules.*
- e. Saturated sodium phosphate solution:* Prepare a saturated solution of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  with cold deionized-distilled water.
- f. Potassium bromide solution, 5%:* Dissolve 5 g KBr and dilute to 100 mL. Store in a brown glass-stoppered bottle. Make fresh weekly.
- g. Hydrochloric acid, HCl, conc.*
- h. Hydrochloric acid, HCl, 2.5N (2.5M):* Cautiously add 200 mL conc HCl, with mixing, to distilled water, diluting to 1000 mL.
- i. Purge gas:* Use nitrogen gas for purging  $\text{ClO}_2$  from samples. Assure that gas is free of contaminants and pass it through a 5% KI scrub solution. Discard solution at first sign of color.

### 4. Procedure

Use either sodium thiosulfate or phenylarsine oxide as titrant. Select concentration on basis of concentration range expected. The total mass of oxidant species should be no greater than about 15 mg. Make appropriate sample dilutions if necessary. A convenient volume for titration is 200 to 300 mL. Preferably analyze all samples and blanks in triplicate.

Minimize effects of pH, time, and temperature of reaction by standardizing all conditions.

*a. Titration of residual chlorine and one-fifth of available  $\text{ClO}_2$ :* Place 1 mL pH 7 phosphate buffer in beaker and add distilled-deionized dilution water if needed. Introduce sample with minimum aeration and add 1 g KI granules while stirring. Titrate to end point (see Section 4500-Cl.D). Record reading  $A = \text{mL titrant/mL sample}$ .

*b. Titration of four-fifths of available  $\text{ClO}_2$  and chlorite:* Continuing with same sample, add 2 mL 2.5N (2.5M) HCl. Let stand in the dark for 5 min. Titrate to end point. Record reading  $B = \text{mL titrant/mL sample}$ .

*c. Titration of nonvolatilized chlorine:* Place 1 mL pH 7 phosphate buffer in purge vessel and add distilled-deionized dilution water if needed. Add sample and purge with nitrogen gas for 15 min. Use a gas-dispersion tube to give good gas-liquid contact. Add 1 g KI granules

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while stirring and titrate to end point. Record reading  $C = \text{mL titrant/mL sample}$ .

*d. Titration of chlorite:* Continuing with same sample, add 2 mL 2.5N (2.5M) HCl. Let stand in the dark for 5 min. Titrate to end point, and record reading  $D = \text{mL titrant/mL sample}$ .

*e. Titration of chlorine,  $\text{ClO}_2$ , chlorate, and chlorite:* Add 1 mL KBr and 10 mL conc HCl to 50-mL reaction flask and mix. Carefully add 15 mL sample, with minimum aeration. Mix and stopper immediately. Let stand in the dark for 20 min. Rapidly add 1 g KI granules and shake vigorously for 5 s. Rapidly transfer to titration flask containing 25 mL saturated  $\text{Na}_2\text{HPO}_4$  solution. Rinse reaction flask thoroughly and add rinse water to titration flask. Final titration volume should be about 200 to 300 mL. Titrate to end point.

Repeat procedure of preceding paragraph using distilled-deionized water in place of sample to determine blank value.

Record reading  $E = (\text{mL titrant sample} - \text{mL titrant blank}) / \text{mL sample}$ .

NOTE: The 15-mL sample volume can be adjusted to provide an appropriate dilution, but maintain the ratio of sample to HCl.

### 5. Calculations

Because the combining power of the titrants is pH-dependent, all calculations are based on the equivalents of reducing titrant required to react with equivalents of oxidant present. Use Table 4500-ClO<sub>2</sub>:I to obtain the equivalent weights to be used in the calculations.

In the following equations,  $N$  is the normality of the titrant used in equivalents per liter and  $A$  through  $E$  are as defined previously.

$$\text{Chlorite, mg ClO}_2^-/\text{L} = D \times N \times 16\,863$$

$$\text{Chlorate, mg ClO}_2^{2-}/\text{L} = [E - (A + B)] \times N \times 13\,909$$

$$\text{Chlorine dioxide, mg ClO}_2/\text{L} = (5/4) \times (B - D) \times N \times 13\,490$$

$$\text{Chlorine, mg Cl}_2/\text{L} = A - [(B - D)/4] \times N \times 35\,453$$

### 6. References

1. AIETA, E.M., P.V. ROBERTS & M. HERNANDEZ. 1984. Determination of chlorine dioxide, chlorine, chlorite, and chlorate in water. *J. Amer. Water Works Assoc.* 76:64.
2. WONG, G. 1982. Factors affecting the amperometric determination of trace quantities of total residual chlorine in seawater. *Environ. Sci. Technol.* 16:11.
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4. JOLLEY, R. & J. CARPENTER. 1982. Aqueous Chemistry of Chlorine: Chemistry, Analysis, and Environmental Fate of Reactive Oxidant Species. ORNL/TM-788, Oak Ridge National Lab., Oak Ridge, Tenn.

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### 7. Bibliography

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**Endnotes**

**1 (Popup - Footnote)**

\* APPROVED BY STANDARD METHODS COMMITTEE, 1993.