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ORION METHOD AC4070

Total and Free Chlorine (Cl_2) by DPD Colorimetry

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Disclaimer

This method has been submitted to the U.S. Environmental Protection Agency for use in EPA's water programs but has not been approved for use by EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Thermo Electron Corporation welcomes suggestions for improvement of this method. Suggestions and questions concerning this method or its application should be addressed to:

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Additional copies of this method may be found at www.thermo.com/waterapps. Follow the link for Colorimetry to this method, Orion AC4070.

Introduction

This method uses self-filling reagent cuvettes (Auto-Test™ cuvette) designed to give quantitative chlorine residual results, which conform with "Standard Methods for the Examination of Water and Wastewater," 20th edition, Method 4500-Cl G and EPA Method 330.5. Use of this Auto-Test™ kit in the laboratory or in the field yields acceptable quantitative analytical results. A standard spectrophotometer or colorimeter is used with the Auto-Test™ cuvette. This test reduces sample and reagent volumes, minimizes hands-on contact with the reagents, and lowers the cost of a chlorine residual analysis.

The method range of 0.15 to 5.0 mg/L Cl_2 encompasses drinking water and wastewater regulatory limitations.

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Orion Method AC4070

Total and Free Chlorine (Cl_2) by DPD Colorimetry

Analyte: Chlorine (CAS # Cl_2 Chlorine 7782-50-5)

1.0 Scope and Application

1.1 The method determines free and total chlorine residual levels on potable waters, municipal wastes, swimming pools, natural and treated waters.

1.2 This method is for use in the United States Environmental Protection Agency's (EPA's) data gathering and monitoring programs under the Clean Water Act and the Safe Drinking Water Act.

1.3 The method detection limit (MDL; 40 CFR 136, Appendix B) has been established at 0.05 mg/L. The Minimum Level (ML) for reporting results is 0.15 mg/L.

1.4 This method is capable of measuring Cl_2 in the range of 0.15 to 5.0 mg/L.

1.5 This colorimetric method determines the presence of Cl_2 in all natural, treated, industrial, waste and drinking water matrices.

1.6 This method is based on prior Environmental Protection Agency (EPA) and associated methods for the determination of Cl_2 (References 16.1 and 16.2).

1.7 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2

2.0 Summary of Method

2.1 Free Cl_2

2.1.1 25ml of a sample is measured into the sample cup.

2.1.2 A reagent filled Auto-Test™ cuvette is placed in the cup, and the tip is snapped against the side of the cup (refer to figure 2).

2.1.3 Free Cl_2 reacts with the DPD color indicator, in the presence of phosphate buffer, to form a red dye.

2.1.4 After a one minute reaction time, the Auto-Test™ cuvette is read on a photometric device.

2.1.5 The photometric measurements are conducted at or near 515 nm.

2.2 Total Cl_2

2.2.1 25ml of sample is measured into the sample cup.

2.2.2 Five drops of Activator Solution are added to the sample, and mixed.

2.2.3 A reagent filled Auto-Test™ cuvette is placed in the cup, and the tip is snapped against the side of the cup (refer to figure 2 of the product instruction sheet).

2.2.4 After a one minute reaction time, the Auto-Test™ cuvette is read on a photometric device.

2.2.5 The photometric measurements are conducted at or near 515 nm.

2.3 Quality is assured through the use of quality control samples (QCS) with each analytical batch. Calibration of the instrumentation can be assured by running calibration test solutions with each analytical batch.

2.4 Analyze all samples immediately after collection.

3.0 Definitions

Definitions for terms used in this method are given in the glossary at the end of the method (Section 18).

4.0 Interferences

4.1 Additional halogens and halogenating agents produce positive

4.2 interferences. Oxidized manganese and ozone are positive

4.3 interferences.

Color and suspended matter may interfere with the photometric measurement. To counter this potential positive interference, use the sample without any addition of reagent as the sample blank.

4.4 Chlorine greater than 500 mg/L will oxidize the DPD to a colorless amine, which can be interpreted as a low chlorine value. Analysts should take note of sample odor, which may indicate high levels of chlorine present.

4.5 High pH levels cause dissolved oxygen to react with the reagents. Very low pH causes a positive free chlorine residual when mono-chloramines are present.

4.6 The test should be conducted between 20 and 25 °C.

5.0 Safety

5.1 This method does not address all safety issues associated with its use. The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets

(MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.4 and 16.5.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring shall be made available to the analyst.

5.3 Samples of unknown origin may possess potentially hazardous compounds. Samples should be handled with care so as to minimize exposure.

5.4 This method employs the use of Auto-Test™ cuvettes, sealed cuvettes containing premixed reagents. This limits the handling of potentially hazardous chemicals.

6.0 Equipment and Supplies

NOTE: *Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Sample collection bottles–100ml to 1-L borosilicate amber glass, or

6.2 plastic Volumetric flasks–various sizes

6.3 Volumetric pipettes–various sizes

6.4 Lint free cloths for cleaning cuvettes

6.5 Temperature probe–capable of measuring between 0 to 40C

6.6 Laboratory timer.

6.7 25ml sample cup

6.8 Photometric device.

6.8.1 Spectrophotometer, for use at a wavelength of 515 nm, with a cell path of 1 cm or longer.

6.8.2 Filter photometer, equipped with a filter having maximum transmission in the wavelength range of 490 - 530 nm, with a cell path of 1 cm or longer.

7.0 Reagents and Standards

7.1 Deionized water – free of Cl_2

7.2 Orion AC4070 Auto-Test™ cuvettes

7.3 Orion AC4070 Activator Solution

7.4 Cl_2 equivalent standard solutions.

7.4.1 Stock Cl_2 standard solution (1000 mg/L):

7.4.1.1 Dissolve 0.89 1 g $KMnO_4$ in a volumetric flask, and dilute to 1 liter. **7.4.2** Intermediate Cl_2 Standard solution (100 mg/L):

7.4.2.1 Prepare a 100 mg/L total Cl_2 intermediate standard by diluting 10 ml of the stock solution to 100 ml with deionized water.

7.4.2.2 Prepare a series of Cl_2 calibration and check standards for chosen measuring range (0.20 - 5.0 mg/L).

7.4.3 Working Cl_2 Standard solution (2 mg/L):

7.4.3.1 Prepare a working standard solution by diluting 2 ml of the intermediate standard solution to 100ml = 2 mg/L of Cl_2. Prepare fresh daily.

8.0 Sample Collection, Preservation, and Storage

8.1 Collect approximately 1 00ml - 1L of representative sample in a plastic or amber glass bottle following conventional grab sampling techniques outlined in Reference 16.7.

8.2 Use preservation and holding time procedures consistent with those specified in current EPA publications or regulations. See 40 CFR 136, Table II.

8.3 Exposure to sunlight, strong light, and agitation will accelerate the reduction of chlorine.

8.4 Collect an additional two aliquots of a sample for each batch (of 20 samples or less) for the matrix spike and matrix spike duplicate.

9.0 Quality Control

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program (Reference 16.6). The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the ongoing analysis of laboratory reagent blanks, precision and recovery standards, and field duplicate samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 Analysis of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure for spiking and for calculating accuracy (P) and precision (RPD) are described in Section 9.6.

9.1.3 Analyses of laboratory reagent water blanks are required to demonstrate freedom from contamination. The procedure and criteria for blank analyses are described in Section 9.3.

9.1.4 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control. These procedures are described in Sections 9.4 and 9.5.

9.1.5 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Section 9.5.3.

9.1.6 Accompanying QC for the determination of Cl_2 is required per analytical batch. An analytical batch is a set of samples analyzed, to a maximum of 20 samples. Each analytical batch, of up to 20 samples, must be accompanied by a reagent water blank (Section 9.3), an ongoing precision and recovery sample (OPR, Section 9.5), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.6).

9.2 Initial demonstration of laboratory capability-The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits.

9.2.1 Method detection limit (MDL)-The method detection limit must be established (as per 40 CFR Part 136, Appendix B) for the analyte, using the Cl_2 standard solution (Section 7.4). To determine MDL values, take seven replicate aliquots of the diluted Cl_2 standard solution and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. MDLs should be determined every year or whenever a modification to the method or analytical system is made that will affect the method detection limit.

9.2.2 Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.2.1 Analyze four samples of the Cl_2 standard (Section 7.4), prepared at the mid-level concentration for the range tested, according to the procedure beginning in Section 11.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (x) and the standard deviation (s, Equation 1) of the percent recovery for Cl_2.

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x^2)}{n}}{n-1}}$$

Where:

n = number of samples

x = % recovery in each sample

s

= standard deviation

9.2.2.3 Compare s and x with the corresponding limits for initial precision and recovery in Table 2. If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.3 Laboratory blanks-Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.3.1 Prepare and analyze a reagent water blank initially (i.e. with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.3.2 If Cl_2 is detected in the blank, at a concentration greater than the ML (Section 1.3), analysis of samples must be halted until the source of contamination is eliminated, and a new blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.

9.4 Calibration verification-Verify calibration of the photometric device per Section 10 for each analytical batch of up to 20 samples. If calibration curve linearity differs more than 10%, run a new calibration curve.

9.5 Ongoing precision and recovery (OPR)-To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:

9.5.1 Analyze a precision and recovery standard (Sections 7.4), prepared at the mid-level concentration for the range tested, with each analytical batch according to the procedure beginning in Section 11.

9.5.2 Compare the concentration with the limits for ongoing precision and recovery in Table 2. If the concentration is in the range specified, the analysis may proceed. If however, the concentration is not in the specified range, the analytical process is not in control. In this event, correct the problem, re-analyze the analytical batch, and repeat the ongoing precision and recovery test.

9.5.3 The laboratory should add results that pass the specification in Section 9.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from R - 2s_r to R + 2s_r.

For example, if R = 95%, and s_r = 5%, the accuracy is 85 % to 105 %.

9.6 Matrix Spikes-The laboratory must spike, in duplicate, a minimum of five percent of all samples (one sample in each batch of 20 samples). The two sample aliquots shall be spiked with the Cl_2 standard solutions (Sections 7.4) diluted to an appropriate level.

9.6.1 The concentration of the spike in the sample shall be determined as follows:

9.6.1.1 If, as in compliance monitoring, the concentration of Cl_2 in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), whichever concentration is higher.

9.6.1.2 If the concentration of Cl_2 in a sample is not being checked against a limit, the spike shall be at the concentration of the precision and recovery standard (Section 7.4), or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.6.2 Analyze one sample aliquot out of each set of 20 samples according to the procedure beginning in Section 11.0 to determine the background concentration (B) of Cl_2.

9.6.2.1 If necessary, prepare a standard solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.6.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A).

9.6.3 Calculate the percent recovery (P) of in Cl_2 each aliquot using the following equation:

Equation 2

$$P = 100 * \frac{(A - B)}{T}$$

where:

P=Percent recovery

A =Measured concentration of Cl_2 after spiking B=Measured concentration of Cl_2 before spiking T=True concentration of the spike

9.6.4 Compare the percent recovery of the Cl_2 with the corresponding QC acceptance criteria in Table 2.

9.6.4.1 If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria in Table 2, (which lists EPA's standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table IB), an interference is present. In this case, the result may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be resampled. If the interference is attributable to a method deficiency, the analyst must modify the method repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS/MSD.

9.6.4.2 If the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample re-analyzed.

9.6.5 Compute relative percent difference (RPD) between the two results (not between the two recoveries) using the following equation:

Equation 3

$$RPD = 100 * \frac{|D_1 - D_2|}{(D_1 + D_2)/2}$$

where:

RPD=Relative percent different

D_1 = Concentration of Cl_2 in the sample

D_2=Concentration of Cl_2 in the second (duplicate) sample

9.6.6 The relative percent difference for duplicates shall meet the acceptance criteria in Table 2, (which lists EPA's standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table IB). If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch re-analyzed.

9.6.7 As a part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples, in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from P_a-2s_p to P_a+2s_p. For example, if P_a = 90% and s_p = 10% for five analyses of Cl_2 the accuracy interval is expressed as 70-110%. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.7 Quality control sample (QCS)–It is suggested that the laboratory obtain a quality control sample from a source different from the source of the Cl_2 used routinely in this method (Sections 7.4).

9.8 The standards used for initial precision and recovery (IPR, Section 9.2.2) and ongoing precision and recovery (OPR, Section 9.5) should be identical, so that the most precise results will be obtained.

10.0 Calibration and Standardization

10.1 Orion AQ4000 colorimeters are shipped factory calibrated, refer to the manufacturer's documents, or call the manufacturer for more information.

10.2 For absorbance mode operation of a spectrophotometer, or with other photometric equipment, plot a calibration curve with a minimum of five (5) data points, from standards prepared from a free or total Cl_2 standard solution (Sections 7.4). The curve should include the lowest and highest concentrations for the range tested (example listed in Section 17, Table 1). The calibration curve should also include a blank. For best results, use linear regression analysis to determine the calibration curve and calculate sample concentration.

10.3 Verify the calibration curve, using a calibration standard, with each analytical batch of samples.(Section 9.4).

10.4 Run a new calibration curve with each new lot of reagents, or when calibration curve linearity differs more than 10%.

11.0 Procedure

11.1 Sample preparation

11.1.1 Check the pH of samples, and if necessary, adjust to pH between 6 and 9.

11.1.2 If the sample contains more than 5 mg/L, dilute into range with chlorine-free deionized water.

11.2 Total Cl_2

Note: Before proceeding with sample analysis, turn on photometric equipment, set the wavelength, and zero the meter. See section 11.4 for Orion AQ4000 instructions or section 11.5 for spectrophotometer or other photometric equipment instructions.

11.2.1 Measure 25 ml of sample into the sample cup.

11.2.2 Add five drops of Chlorine Activator solution AC4070 into the sample cup and stir briefly with the tip of the cuvette.

11.2.3 Wait one minute.

11.2.4 Place the Auto-Test™ cuvette into the sample cup with the tip down. Snap the tip by pressing the cuvette against the side of the sample cup. The cuvette will fill, leaving a small bubble to facilitate mixing.

11.2.5 Mix the contents of the cuvette by inverting it several times, allowing the bubble to travel the entire length of the tube. Tap the bottom of the cuvette on a hard surface to cause any tiny bubbles that have collected on the cuvette wall to rise to the top.

11.2.6 Wipe all liquid from the exterior of the cuvette.

11.2.7 Proceed to section 11.4 for use with Orion AQ4000 colorimeter or section 11.5 for use with spectrophotometer or other photometric equipment.

11.3 Free Cl_2

11.3.1 Repeat 11.2, omitting steps 11.2.2 and 11.2.3.

11.4 Determination using Orion AQ4000 colorimeter

11.4.1 Switch on the Orion AQ4000 colorimeter as per manufacturer's suggestions.

11.4.2 It is not necessary to set the wavelength on the Orion AQ4000. The instrument automatically selects Program #22 for chlorine analysis when the Auto-Test™ cuvette is inserted into the colorimeter, loading the appropriate wavelength, measuring parameters, and calibration.

11.4.3 Zero the instrument with a sealed zero vial from the Orion AQUAfast® IV Zero Auto-Test™ kit, AQ4ZER. For colored or turbid samples, prepare a sample blank as follows: 1) Add 10 ml of sample and 5 mL of DI water to a sample cup for a total of 15 mL. 2) Transfer a portion of the diluted sample to a clean, dry 13mm vial (as provided in AQ4ZER) and use that vial to zero the meter. Discard the diluted sample after the zero procedure. Repeat for every colored or turbid sample. Rezero with the sealed zero vial before testing any clear, colorless samples.

11.4.4 Follow the test procedure as outlined in 11.2.1 through 11.2.6.

11.4.5 Place the cuvette into the colorimeter. Align the –on the Auto-Test™ cuvette with the — on the adapter to obtain a continuous beeping and view * * * ** * * * across the display. If * * * * * * * * and beeping are not observed, rotate cuvette right or left to initiate the measurement.

11.4.6 Immediately cover the cuvette with the cuvette cover. The Orion AQ4000 will begin a 1-minute countdown. After the countdown is completed, the Orion AQ4000 will automatically proceed to the measure mode.

11.4.7 Record the concentration reading from the Orion AQ4000 display as either mg/L or ppm Cl_2, or log measurement into the data logger by pressing the log key.

11.5 Determination using a spectrophotometer or other photometric equipment.

11.5.1 Warm up the instrument as per manufacturer's suggestion for

operation.

11.5.2 Set the instrument to a wavelength of 515 nm.

11.5.3 Zero the instrument with deionized water. For colored or turbid samples, prepare a sample blank as follows: 1) Add 10 ml of sample and 5 mL of DI water to a sample cup for a total of 15 mL. 2) Transfer a portion of the diluted sample to a clean, dry 13mm vial and use that vial to zero the meter. Discard the diluted sample after the zero procedure. Repeat for every colored or turbid sample. Rezero with the sealed zero vial before testing any clear, colorless samples.

11.5.4 Follow the test procedure as outlined in 11.2.1 through 11.2.6.

11.5.5 Allow one minute for color development, then place the cuvette into the photometer.

11.5.6 Record the absorbance reading from the instrument.

11.5.7 Plot the absorbance reading from the sample against the calibration curve, to obtain the concentration Cl_2 as mg /L.

12.0 Data Analysis and Calculations

12.1 If no pre-dilution was performed upon the sample, no calculation is necessary.

12.2 If pre-dilution was required, calculate the Cl_2 (mg /L) as follows:

Equation 3

$$Cl_2 = A * \frac{V_2}{V_1}$$

where:

A = Measured concentration of Cl_2 from photometric determination (mg/L)

V_1 = Volume of sample used for dilution (ml)

V_2 = Final total volume of diluted sample (ml)

12.3 Report results to two significant digits for concentrations found above the ML (Section 1.3) in all samples. Report results below the ML as <0.15 mg/L for Cl_2.

13.0 Method Performance

13.1 This method, as equivalent to Standard Method 4500-Cl G (Reference 16.1), should achieve the same method performance, as cited by the reference method.

13.2 The method detection limit (MDL) study was performed by a single analyst, and was determined as 0.05 mg/L.

13.3 The minimum level (ML) is determined as 0.15 mg/L.

14.0 Pollution Prevention

14.1 The reagents used in this method pose little threat to the environment, when managed properly.

14.2 The DPD oxalate is toxic, avoid ingesting any of the vial contents.

14.3 Reagents should be ordered consistent with laboratory use, to minimize the amount of expired materials to be disposed.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restriction. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations.

15.2 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better: Laboratory Chemical Management for Waste Reduction," both available from the American Chemical Society's Department of Government
Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

16.0 References

16.1 "Standard Methods for the Examination of Water and Wastewater," 20th Edition, American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005, Method 4500-Cl G.

16.2 "Methods for the Chemical Analysis of Water and Wastes," 3rd Edition, Environmental Protection Agency, Environmental Monitoring Systems Laboratory–Cincinnati (EMSL–Ci), Cincinnati, Ohio 45268, EPA–600/4-79-020, Method 330.5.

16.3 Orion AQUAfast® IV Auto-Test™ cuvette instruction sheet.

16.4 "OSHA Safety and Health Standards, General Industry," (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

16.5 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

16.6 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.7 "Standard Methods for the Examination of Water and Wastewater," 20th Edition, American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005, Method 1060.

17.0 Tables

Table 1. Calibration Standard Preparation

Concentration Range (mg/L)	100 mg/L Intermediate Standard Solution (ml) diluted to 100ml	Concentration of Curve Standards (mg/L)
0.15 - 5.0	0 - 0.15 - 1.0 - 2.0 - 3.5 - 5.0	0.15 - 1.0 - 2.0 - 3.5 - 5.0

Table 2. Acceptance Criteria for Performance Tests

Acceptance Criteria	Section	Limit (%)
Initial Precision and Recovery	9.2.2	
Cl_2 Precision (s)	9.2.2.2	19
Cl_2 Recovery (R)	9.2.2.2	82-120
Matrix Spike	9.6	
Cl_2 RPD	9.6.5	21
Cl_2 Recovery	**9.6.3**	80-122
Ongoing Precision and Recovery	9.5	
Cl_2 Recovery	9.5	80-122

18.0 Definitions

18.1 The definitions and purposes are specific to this method, but have been conformed to common usage as much as possible.

18.1.1 Symbols

°C	degrees Celsius
>	greater than
<	less than
%	percent

18.1.2 Alphabetical Characters

g	gram
L	liter
mg	milligram
mg/L	milligram per liter
ml	milliliter
nm	nanometer
µg	microgram

18.2 Definitions, acronyms, and abbreviations.

18.2.1 Analyte: Chlorine (Cl_2), which is determined by this method.

18.2.2 Analytical batch: The set of samples analyzed at the same time, to a maximum of 20 samples. Each analytical batch must be accompanied by a laboratory blank (Section 9.3), and ongoing precision and recovery sample (OPR, Section 9.5), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.6).

18.2.3 Auto-Test™ cuvette Orion AQUAfast® IV: The reagent test kit which incorporates pre-measured reagents for field measurement of the various forms of Cl_2.

18.2.4 Bound chlorine: Cl_2 that is present in the form of chloramines and organic chloramines.

18.2.5 Bound Cl_2: See bound chlorine.

18.2.6 Free Chlorine: The portion of Cl_2 which is present in water in the form of dissolved elementary Cl_2, as hypochlorous acid and the hypochlorite ion.

18.2.7 Free Cl_2: See free chlorine.

18.2.8 IPR: See initial precision and recovery.

18.2.9 Initial precision and recovery (IPR): Four aliquots of the diluted Cl_2 standard are analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrument is modified.

18.2.10 Laboratory reagent water blank (method blank): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The laboratory blank is used to determine if analyte or interferences are present in the laboratory environment, or the reagents.

18.2.11 Matrix spike (MS) and matrix spike duplicate (MSD): Aliquots of environmental sample to which known quantities of the analyte are added in the laboratory.

The MS and MSD are prepared and/or analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

18.2.12 May: This action, activity, or procedural step is neither required nor prohibited.

18.2.13 Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

18.2.14 Minimum level (ML): The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point of the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and preparation procedures have been employed.

18.2.15 Must: This action, activity, or procedural step is required.

18.2.16 OPR: See ongoing precision and recovery standard.

18.2.17 Ongoing precision and recovery standard (OPR): A laboratory blank spike with known quantities of analyte. The OPR is treated exactly like a sample. Its purpose is to establish performance of the method by the analyst.

18.2.18 Orion AQ4000 Colorimeter: Portable colorimeter which automatically sets the appropriate measuring parameters including wavelength, color development time, and calibration data.

18.2.19 Quality Control Sample (QCS): A sample containing analyte of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that heave been prepared independently from the normal preparation process.

18.2.20 Reagent water: Water demonstrated to be low or free from chlorine.

18.2.21 Shall: This action, activity, or procedural step is required.

18.2.22 Should: This action, activity, or procedural step is suggested, but not required.

18.2.23 Total Chlorine: The sum of free and bound chlorine as defined is Sections 18.2.4 and 18.2.6.

18.2.24 Total Cl_2: See total chlorine.