METHOD 1.00598Cl_2

Chlorine (Cl_2) by DPD and Photometry

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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.

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Introduction

This method is a convenient ready to use chlorine test kit for free chlorine testing which is based on "Standard Methods for the Examination of Water and Wastewater," 18th edition, Method 4500-Cl G and EPA Method 330.5, and International Standard Organization (ISO) Method 7393. This method is equivalent to Method 14828Cl_2 which is approved by EPA Waste Water Committee as equivalent to Method 4500-Cl G and EPA Method 330.5.

The test kit is suitable for both on-site testing and typical laboratory testing. The test kit consists of pre-measured reagent sets for analytical determinations. This method's approach with pre-measured reagents reduces the analytical errors, the amount of hazardous waste and increases occupational safety.

The method incorporates a range of 0.01 to 7.50 mg/L free Cl_2. This broad range helps to reduce the amount of sample manipulation, especially in field applications.

Method 1.00598Cl_2

Chlorine (Cl_2) by DPD and Photometry

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

1.0 Scope and Application

1.1 This photometric method determines the concentration of free chlorine (Cl_2). In the absence of iodide ions, free Cl_2 (hypochlorous acid and hypochlorite ions) react instantly with Dialkyl-p-phenylenediamine to form a red dye. The intensity of the color formed in both cases is measured photometrically.

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 0.010 mg/L using a 50 mm rectangular cell (Section 13.2). The Minimum Level (ML) for reporting results is 0.010 mg/L using a 50 mm rectangular cell (Section 13.3).

1.4 This method is capable of measuring free Cl_2 in the range of 0.010 to 7.50 mg/L.

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

1.6 This method is based on prior Environmental Protection Agency (EPA) and association 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 The pH of new samples is checked. If the pH is outside the range of four to eight, adjust with dilute sodium hydroxide or sulfuric acid.

2.2 An eight-ml aliquot of the sample is transferred to a 16 x 100-mm test tube (Section 17, Table 1).

2.3 N,N-Di-n-propyl-1,4 phenylenediamine DPD color indicator/EDTA buffer mixture (Spectroquant® Reagent Cl_2-1) is added to adjust the pH of the sample to 5.0 ± 0.5. Free Cl_2 reacts with the DPD color indicator to form a red dye.

2.4 After a one minute reaction time, the solution is added to a cuvette for photometric measurement.

2.5 The photometric measurements are conducted at or near 557 nm on a photometric device.

2.6 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.

2.7 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 Cyanide, dichromate, nitrite and sulfide ions interfere in concentrations >0.1 mg/L.

4.2 Bromine and iodine interfere in concentrations > 0.5 and >0.7 mg/L respectively.

4.3 Hydrogen peroxide interferes in concentrations > 0.05 mg/L.

4.4 Ozone interferes at concentration above 0.1 mg/L.

4.5 Chlorine dioxide interferes in concentrations greater than 0.2 mg/L.

4.6 At low pH levels, monochloramine reacts as free Cl_2. Adjust the pH of new samples to between four and eight. The EDTA buffer of Spectroquant® Reagent Cl_2-1 ensures that the optimal pH conditions of 5.0 ± 0.5 are maintained throughout the test (Reference 16.3).

4.7 Adjust extremely basic samples to a pH of 4-8 with diluted sulfuric acid. The EDTA buffer of Spectroquant® Reagent Cl_2-1 ensures that the optimal pH conditions of 5.0 ± 0.5 are maintained throughout the test procedure (Reference 16.3).

4.8 Temperatures higher than 40ºC increases the tendency for chloramines to react, which can cause increased free Cl_2 results. Conduct test procedure on samples between 5 and 40ºC.

4.9 An overview of other interfering ions up to concentrations of 1000 mg/L in solutions containing 3.5 and 0 mg/L Cl_2 is given in Reference 16.4.

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 16.5 and 16.6.

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 This method employs the use of Cl_2 test kits, which consist of 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–1-L borosilicate amber glass, or plastic.

6.2 Volumetric flasks–various sizes.

6.3 Volumetric pipettes–various sizes.

6.4 Analytical Balance–capable of weighing 0.1 mg.

6.5 Standard test tubes–16 x 100 mm.

6.6 Rectangular cuvettes–10 mm, 20 mm, and 50 mm.

6.7 Temperature probe–capable of measuring between 0 to 40ºC.

6.8 Laboratory timer.

6.9 Rack for tubes–16 x 100 mm.

6.10 Dry cloths for cleaning cuvettes.

6.11 Photometric device.

6.11.1 Photometer, with maximum transmittance at a wavelength near 557 nm, cell path of 1 cm or longer, and cell compartments for round cells and rectangular 10-mm, 20-mm, and 50-mm cuvettes–Spectroquant®-type system photometer (References 16.6, 16.7, and 16.8), or equivalent.

6.11.1.1 AutoSelector device - provided with the Spectroquant® Chlorine Test.

6.11.2 Spectrophotometer, for use at a wavelength of 557 nm, with cell path of 1 cm or longer, and cell compartment for round cells and rectangular 10-mm, 20-mm, or 50-mm cuvettes.

7.0 Reagents and Standards

7.1 Deionized water – free of Cl_2.

7.2 N,N-Di-n-propyl-1,4-phenylenediamine/EDTA buffer mixture - Spectroquant® Reagent Cl_2-1.

7.3 Free Cl_2 stock standard

7.3.1 Prepare a 1:10 dilution (e.g., 10 ml:100 ml) of sodium hypochlorite solution containing approximately 13% of active Cl_2 (catalog no. 1.05614.9025, or equivalent).

7.3.2 With a volumetric pipette, measure 5.00 ml of this 1:10 solution into a 250-ml Erlenmeyer flask containing 30 ml of deionized water.

7.3.3 Immediately and add 5.0 ml of 100% acetic acid and 2.0 g of potassium iodide. Quickly seal flask and mix to dissolve. Allow five minutes for reaction.

7.3.4 Free iodine will be released, and the mixture will turn yellow to brown. Titrate the iodine, with 0.1N sodium thiosulfate solution (catalog no. 1.09147, or equivalent), to a pale yellow. Add two ml of zinc iodide-starch solution (catalog no. 1.05043, or equivalent). Titrate from blue to colorless.

7.3.5 Calculate the mg of free Cl_2 in this 5-ml volume of the 1:10 solution as follows:

ml of titrant (catalog no. 1.09147, or equivalent) x 3.55 = mg free Cl_2

7.4 100 mg/L free Cl_2 standard.

7.4.1 Divide 100 mg by the mass (mg free Cl_2) as determined in 7.5.1.5. Multiply this factor by the five-ml volume of solution used to determine the volume of this 1:10 solution which must be diluted to 1L to give a 100 mg/L free Cl_2 standard.

7.4.2 Measure this calculated volume of the calibrated 1:10 dilution, from the remaining 100 ml of 1:10 solution, to obtain a 100 mg/L standard of free Cl_2..

7.4.3 Prepare a series of free Cl_2 standards for the chosen measuring range (Section 17, Table 2). Diluted standards for free Cl_2 are stable at room temperature for one hour. Always prepare freshly from the calibrated 1:10 solution.

8.0 Sample Collection, Preservation, and Storage

8.1 Collect approximately 100 ml of representative sample in a plastic or amber glass bottle following conventional grab sampling techniques outlined in Reference 16.10.

8.2 Analyze all samples for Cl_2 immediately after sampling, 40 CFR 136, Table II.

8.3 Exposure to sunlight, strong light, and agitation should be avoided.

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 16.11). 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 7.4.3). 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 7.4.3), 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 (Section 7.4.3, and Section 17, Table 2), prepared at the mid-level concentration for the range tested, with each analytical batch according to the procedure beginning in Section 11.0.

9.5.2 Compare the concentration with the limits for ongoing precision and recovery in Section 17.0, Table 3. 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 7.4.3) 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 7.4.3), 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 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 3.

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 3, (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

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

where:

RPD=Relative percent different

D_1=Concentration of Cl_2 in the spiked sample

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

9.6.6 The relative percent difference for duplicates shall meet the acceptance criteria in Table 3, (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 (Section 7.4.3).

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 Merck Spectroquant®-type system photometer is shipped factory calibrated (Reference 16.12), refer to the manufacturer's documents (References 16.7, 16.8, and 16.9). The calibration curve can be verified, and the data from this verification can be stored, modified or re-entered at anytime. However, the factory program settings cannot be changed by the user. When appropriate, the manufacturer supplies a new MemoChip (transponder) containing new calibration data. An AutoSelector device, placed in the round cell compartment, sets the wavelength and other measuring parameters (i.e. method, type of cell, method calibration data).

10.2 For absorbance mode operation of Merck Spectroquant-type system photometer, or with other photometric equipment, plot a calibration curve with a minimum of five (5) data points, from standards prepared from a free Cl_2 standard solution (Section 7.4.3). The curve should include the lowest and highest concentrations for the range tested (Section 17, Table 2). The calibration curve should also include a blank.

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 Check the pH of samples, and if necessary, adjust to pH between four and eight.

11.2 With a volumetric pipette, add 8.0 ml of sample to a round cell test tube.

11.3 Add one dose (100 mg) of Spectroquant® Reagent Cl_2-1.

11.4 Shake the tube vigorously to dissolve the solid substance.

11.5 Set aside for one minute.

11.6 Choose the appropriate rectangular cuvette size depending upon the limit of detection required (Section 17.0, Table 1).

11.7 Pour contents into the cuvette, and wipe sides of the cuvette with a dry cloth.

11.8 Determination using Merck Spectroquant®-type photometer (References 16.7, 16.8, and 16.9).

11.8.1 Switch on the Merck Spectroquant®-type photometer as per manufacturer's suggestions for operation (References 16.7, 16.8, and 16.9).

11.8.2 Place the AutoSelector in the cell compartment, with the line facing you. The instrument sets automatically to the appropriate wavelength and measuring parameters (bar code recognition, item number, test range, cell format, wavelength, and calibration data).

11.8.3 Place the cuvette into the cuvette compartment.

11.8.4 Record the displayed result in mg/L.

11.9 Determination using absorbance mode of Merck Spectroquant®-type photometer, or other photometric equipment.

11.9.1 Warm up the instrument as per manufacturer's suggestion for operation.

11.9.2 Set the instrument to a wavelength at or near 557 nm, or use filter near 557 nm.

11.9.3 Zero the instrument with a reagent water blank, which has been prepared in the same manner as the standards and samples.

11.9.4 Place the cuvette into the cuvette compartment.

11.9.5 Record the absorbance reading from the instrument.

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

11.10 The range of the test can be expanded by doubling both the sample and reagent volumes as outlined in Section 17.0, Table 1.

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 4

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

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 three significant digits for concentrations found above the ML (Section 1.3) in all samples. Report results below the ML as <0.010 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 0.010 mg/L.

13.3 The minimum level (ML) is determined as 0.010 mg/L **using a 50 mm rectangular cell.**

14.0 Pollution Prevention

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

14.2 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," 18th 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 Spectroquant® Package Insert Catalog Number 14828, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release April 1999.

16.4 Spectroquant® Package Insert Catalog Number 1.00598, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release March 2000.

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

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

16.7 Spectroquant® SQ118 Manual, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany.

16.8 Spectroquant® NOVA 60 Manual, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release July 1998.

16.9 Spectroquant® NOVA 400 Manual, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany.

16.10 "Standard Methods for the Examination of Water and Wastewater," 18th Edition, American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005, Method 1060.

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

16.12 "German Standard Methods for the Examination of Water, Wastewater, and Sludge," Deutsches Institut fhr Normung e.V., D-10772, Berlin, DIN Method 38408 Part 4, May 1986.

17.0 Tables

Table 1. Product Range and Usage Information

Concentration Range (mg/L)	Sample Volume (ml)	Cuvette Size (mm)
0.010 - 1.500	8	50
0.05 - 4.00	8	20
0.10 - 7.50	8	10

Table 2. Calibration Standard Preparation

Concentration Range (mg/L)	100 mg/L Standard Solution (ml)	Concentration of Curve Standards (mg/L)
0.10 - 7.50	0 - 0.1 - 1.0 - 2.5 - 5.0 - 7.5 (dilute to 100 ml)	0 - 0.1 - 1.0 - 2.5 - 5.0 - 7.5
0.05 - 4.00	0 - 0.05 - 0.5 - 1.0 - 2.5 - 4.0 (dilute to 100 ml)	0 - 0.05 - 0.5 - 1.0 - 2.5 - 4.0
0.010 - 1.500	0 - * - 0.5 - 0.75 - 1.0 - 1.5 (dilute to 100 ml)	0 - 0.01 - 0.5 - 0.75 - 1.0 - 1.5

* for 0.01 mg/L, dilute 10 ml of 100 mg/L standard to 1L (1ml = 1 µg). Dilute 1.0 ml to 100 ml (0.01 mg/L standard).

Table 3. Acceptance Criteria for Performance Tests

Acceptance Criterion	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	21
Cl_2 Recovery		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 AutoSelector device: The device which, when placed in the cell compartment, will set the Merck Spectroquant®-type photometer to the appropriate chlorine measurement settings (wavelength, calibration, etc.).

18.2.4 Bound chlorine: Cl_2 which is present in water 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 MemoChip: See transponder.

18.2.14 Merck Spectroquant®-type system photometer: Photometers containing information on Spectroquant® products. The instrument automatically sets to the appropriate wavelength and measuring parameters through bar code recognition of item, indicating item number, test range, cell format, wavelength, and calibration data.

18.2.15 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.

18.2.16 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.

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

18.2.18 OPR: See ongoing precision and recovery standard.

18.2.19 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.

18.2.20 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.

18.2.21 Reagent water: Water demonstrated to be low or free from organic matter.

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

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

18.2.24 Spectroquant® Cl_2 Cell Test 1.00598: The test kit which incorporates pre-measured reagents for field measurement of the various forms of Cl_2.

18.2.25 Total chlorine: The sum of free and bound chlorine as defined in Sections 18.2.4 and 18.2.6.

18.2.26 Total Cl_2: See total chlorine.

18.2.27 Transponder: The MemoChip, which contains updated information which may include new methods and updated calibration information for downloading into the Merck Spectroquant®-type system photometers.