Comparison Table

SM 4500-Cl G	Merck 1.00595Cl_2 – March 2000
1.0 Scope and Application	**1.0 Scope and Application**
This photometric method determines the presence of total and free chlorine in natural, treated, industrial, waste waters and drinking waters. **Free Chlorine** In the absence of iodide ion, free chlorine (hypochlorous acid, and hypochlorite ions) reacts instantly with N, N-Diethyl-p- phenylenediamine (DPD) under neutral pH conditions to produce a red color. The color's intensity can be measured photometrically at 515 nm. This method is capable of measuring chlorine in the range of 0.05-5 mg/L. Diluting sample when chlorine exceeds 5 mg/L could increase this range. **MDL** The Method Detection Limit (MDL) for this method, under optimum conditions is 0.018 mg/L. **ML** The Mimimum Level (ML) for this method is 0.05 mg/L. This method is applicable for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act.	This photometric method determines the presence of total and free chlorine in drinking, natural, treated, industrial, and wastewaters. **Free Chlorine** In the absence of iodide ions, free and bound chlorine react instantly with N,N- Dipropyl-p-phenylenediamine, within a pH range of 5.0±0.5, to form a red dye. The color's intensity can be measured photometrically at or near 557 nm. The red dye, which is formed, has two maximum absorbances, 515 nm and 557 nm. At the 557-nm wavelength, the optimum absorbance is 15% higher for this compound. N,N-Dipropyl-p-phenylenediamine, is a compound which forms a red color complex like the compound formed by DPD. The compound formed by this method offers an increased stability over time versus the stability of the DPD compound. This method is capable of measuring chlorine in the range of 0.05-7.50 mg/L. Diluting the sample (prior to reagent addition), when chlorine exceeds this maximum range, can also expand the range further. **MDL** The Method Detection Limit (MDL) is established at 0.05 mg/L. **ML** This method can achieve a ML of 0.05 mg/L. This 0.05 mg/L ML is equivalent to the ML for the standard reference method (SM 4500-Cl G). This method is applicable for use in the Environmental Protection Agency's EPA's survey and monitoring programs under the Clean Water Act and the Safe Drinking Water Act.

2.0 Summary of Method	**2.0 Summary of Method**
For this photometric method a photometer is calibrated at 515 nm with standards made from chlorine or potassium permanganate solutions. The curve is prepared using at least five standards and a blank. A sample aliquot that will adequately fill the appropriate photometric cell is measured from a fresh sample. The sample should not be exposed to light or agitation. Buffer and DPD color reagents are added to the sample. Sample and reagents are mixed, allowed to stand, and are then read on the photometer at 515 nm immediately. If samples exceed 5 mg/L, they can be diluted with chlorine free water. Samples can be compared to color standards and a standard can be run to check calibration.	A 5-ml aliquot of pH adjusted sample (pH 4-8) is pipetted into a Spectroquant®- Cl_2 Cell test tube . Solid test reagents consisting of an N,N-dipropyl-p-phenylenediamine-EDTA-buffer mixture and potassium iodide solution (included as pre-mixed reagents) is added to the sample, according to the protocol (depending upon the sample volume tested). Sample and reagents are mixed, and after a one-minute reaction time, the solution is read on a Merck Spectroquant®-type system photometer at or near 557 nm. The Merck Spectroquant®-type system photometers are factory calibrated. Calibration standards and outside control standards can be run to check the instrument calibration. Samples, analyzed using other photometric devices, are compared to a standard calibration curve. If samples exceed 7.50 mg/L, the samples can be diluted prior to analysis with chlorine free water to expand the measuring range.
3.0 Definitions	**3.0 Definitions**
See section 18.0 – There is no listed terminology, acronyms, or symbols which have been defined in this method.	See section 18.0. This method, in great detail, defines terminologies, acronyms, and symbols, which appear in the body of the method. The method incorporates into the body of the method, a detailed quality control section. Many of the terms defined in the glossary are specific to the quality control sample requirements of the method.
4.0 Interferences	**4.0 Interferences**
High concentrations of monochloramine interfere with free chlorine determination but this interference can be overcome by the addition of arsenite or thioacetamide. Oxidized forms of manganese can interfere with chlorine. Using a blank can compensate for this interference. Nitrogen trichloride may react partially as free chlorine, but this interference does not appear to be significant. Sample color and turbidity may interfere and can be compensated by using a sample blank. Organic contaminants may produce a false free chlorine reading, therefore a differentiation between free and	Cyanide, dichromate, nitrite, and sulfide ions interfere in concentrations greater than 0.1 mg/L. Hydrogen peroxide interferes in concentrations above 0.05 mg/L. Ozone interferes in concentrations over 0.01 mg/L. Chlorine dioxide interferes in concentrations greater than 0.2 mg/L. Bromine interferes at levels above 0.5 mg/L. Extremely basic samples should be adjusted to pH between 4 – 8. The EDTA buffer of Spectroquant®

combined chlorine is seldom made in wastewaters. Drinking water, which is typically free of organic contaminants, is usually analyzed for free chlorine, therefore, there are no significant interferences from organic contaminants. Waters containing iodine-reducing agents may not be analyzed for total chlorine since the method depends on the production of iodine. Interference from copper occurring up to approximately 10 mg Cu^{2+}/L is overcome by the addition of EDTA. Chromate in excess of 2 mg/L Cr^{6+} can interfere, but is easily masked by the addition of barium chloride. Iodide contamination in glassware can occur but can be avoided by rinsing thoroughly between samples or using dedicated glassware. Accurate results can only be generated on samples with a neutral pH. A low pH will allow monochloramine to react as free chlorine, while a high pH allows dissolved oxygen to react. Samples must be adjusted to a pH of 6.2 ± 0.5 with dilute sodium hydroxide or dilute sulfuric acid. High temperatures increase the tendency for chloramines to react, which can result in false positive free chlorine results. High temperatures also decrease color intensity. The temperature of the sample should be between 5 and 40 °C.	Reagent Cl_2-1 ensures that the optimal pH of 5.0 ± 0.5 is maintained throughout the test procedure. 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 The reference method does not define any potential health risks associated with the use of the chemicals in this method.	**5.0 Safety** This method employs the use of premixed reagents, hence the handling of hazardous chemicals is significantly reduced. As with any analytical procedure, the analyst is cautioned to become familiar with the potential health hazards described in the reference Material Safety Data Sheet (MSDS) records. Each chlorine reagent test is also clearly labeled with the contents, and any potential health hazards. These help to insure the safety of the analysts involved in the procedure.

6.0 Equipment and Supplies	**6.0 Equipment and Supplies**
This method employs standard laboratory glassware for sampling (1L glass or plastic bottle). Standard glassware for sample and reagent handling includes pipettes, flasks, and photometric cells. A spectrophotometer for use at 515 nm or a filter photometer equipped with a filter accommodating wavelength range of 490-530 nm is used to measure the concentration of chlorine.	This method employs all equipment and supplies which are specified in SM 4500-Cl G. The photometric determination is accomplished using a Merck Spectroquant®-type system photometer or other photometric device. The wavelength maximum absorbance is achieved at or near 557 nm. **Spectroquant® Cl_2 Cell test tubes** This method employs Spectroquant® Cl_2 Cell test tubes. **Merck Spectroquant® -Type System Photometer** Chlorine test identification – A bar coded cell test tube is inserted into the Merck Spectroquant® -type system photometer round cell compartment. The bar code information sets the wavelength and other measuring parameters; method, type of cell, and method calibration data. The readings obtained from the samples are automatically expressed as the chlorine concentration in mg/L. Calibration - The Merck Spectroquant® -type system photometers have been factory calibrated, and the readings obtained from the samples are automatically expressed as the chlorine concentration mg/L. The calibration curve can be verified, and the data from this verification can be stored, modified or re-entered at any time. However, the user can not change the factory program settings. When appropriate, the manufacturer supplies a new MemoChip (transponder) containing new calibration data. **Other Photometric Devices** The use of other photometric equipment, which may be substituted for use with this method, is consistent with the reference method specifications. All photometric measurements, regardless of instrument used, are read at or near the wavelength of 557 nm. (See Appendix I). This wavelength is one of the maximum absorbance wavelengths of the color complex formed during this procedure. The 557-nm wavelength offers increased time stability over the DPD color complex, and the optimum absorbance at this wavelength is 15% greater than at 515 nm.

7.0 Reagents and Standard This method incorporates the following chemicals which are prepared by the laboratory analyst: Phosphate buffer solution N, N-Diethyl-p-phenylenediamine (DPD indicator solution) Standard ferrous ammonium sulfate (FAS) titrant Potassium iodide, KI, crystals Potassium iodide solution Sodium arsenite solution Thioacetamide solution Chlorine standard solutions (acetic acid, KI, Sodium Thiosulfate titrant, phosphate buffer, DPD indicator, FAS titrant) Potassium permanganate standard solutions	**7.0 Reagents and Standards** This method incorporates chemicals similar to SM 4500-Cl G. The indicator solution, N,N-Di-propyl-1,4-phenylenediamine, is used in this method versus N, N-Di-ethyl-p-phenylenediamine, which is used in the standard reference method. The DPD derivative N,N-Di-propyl-1,4-phenylenediamine is used in Method 14828Cl$_2$, which EPA designated equivalent to Method 4500-Cl G and EPA Method 330.5. This DPD derivative forms a more stable color complex at the higher chlorine concentration range of this method. The color complex is stable for extended periods of time. The increased color stability of the N,N-Di-propyl-1,4-phenlyenediamine is illustrated in Appendix II. The reagents, listed in the SM 4500-Cl G, are prepackaged, and added to the test sample according to the protocol (See section 11.0). The chlorine standard solutions are prepared according to the SM 4500-Cl G. The chlorine standards are incorporated into the quality control sample program, as initial precision and recovery (IPR), ongoing precision and recovery (OPR), and for calibration curve verification.
8.0 Sample Collection, Preservation, and Storage The sampling is performed in accordance with Standard Methods. The sample is collected (preferably), in a glass bottle. Because of the small sample volumes used, the sample must be homogenized prior to delivery into the reaction cells. The samples should be stored at 4^{o}C until analysis.	**8.0 Sample Collection, Preservation, and Storage** The sampling is performed in accordance with Standard Methods. There are no differences in the way the samples are collected, preserved or stored in this method.

9.0 Quality Control There are no quality control guidelines incorporated into the body of this method.	**9.0 Quality Control** This method includes guidelines for initial demonstration of laboratory capability, quality control and quality assurance measurements. Initial demonstration of performance of the method is required. After initial performance has been established, the analyst is required to provide proof of continued performance through the analysis of ongoing precision and recovery standards. These are tested in conjunction with the entire analytical quality control batch (for up to 20 samples), which include: (1) laboratory blank, (1) laboratory control sample (OPR), (1) sample in duplicate And a sample spiked in duplicate (MS/MSD). This method requires that a laboratory using this method must operate a formal quality assurance program.
10.0 Calibration and Standardization The spectrophotometer is calibrated using a blank and at least five (5) chlorine standards covering the concentration range of samples to be tested. The absorbance of the each standard is plotted against the concentration. Absorbance readings from samples are plotted against this curve to obtain a concentration value. The calibration curve should be re-run if the linearity of the curve varies more than 5%, or with each new lot of reagents.	**10.0 Calibration and Standardization** **Merck Spectroquant® -Type System Photometer** The Merck Spectroquant®-type system photometers are factory calibrated with standard reference material, and the products are shipped with Lot Certificates for calibration. The factory calibration can be checked, as described in SM 4500-Cl G. **Other Photometric Devices** The calibration is performed as described in SM 4500-Cl G. Calibrate the analytical balance (for weighing solid reagents for standard preparation) with class S certified weights.

11.0 Procedure	**11.0 Procedure**
A 10-ml volume of fresh sample is measured. Alternate sample volumes may be utilized, however, the reagent additions must be adjusted accordingly. The buffer reagent and DPD are added to the sample, and color is developed in the sample. The color's intensity is measured at 515 nm to determine free chlorine. With the addition of varying amounts of KI, and recording absorbance measurements after the additions, monochloramine, dichloramine, and nitrogen trichloride concentrations may be determined separately. Total chlorine can be calculated by adding these concentrations	The pH of samples is checked and, where necessary, adjusted with dilute sodium hydroxide or dilute sulfuric acid (to pH between 4 – 8). A 5-ml volume of fresh sample is transferred to a Spectroquant® Cell test tube. Depending on the type of chlorine tested, pre-mixed reagents (Section 7) are added to the test sample similar to the SM 4500-Cl G. The Spectroquant® reagent formulations are consistent with those cited in the reference method (see N,N-Di-propyl-1,4-phenylenediamine, Appendix II). The photometric measurements are conducted at or near 557-nm using a Merck Spectroquant®-type system photometer, or other photometric device. The 557-nm wavelength is a maximum absorbance range for N,N-Di-propyl-1,4-phenylenediamine (Reference 16.3). The use of N,N-Di-propyl-1,4-phenylenediamine offers a higher sensitivity and stability of the red dye complex, as compared to N,N-Di-ethyl-p-phenylenediamine (read at 515 nm) described in SM 4500-Cl G (See Appendix I and Appendix II). If samples exceed the listed measuring range, dilution of the sample, with chlorine free reagent water (before reagent addition), increases the working range. This method is capable of measuring chlorine in the range of 0.05 – 7.50 mg/L using a Merck Spectroquant® -type system photometer. The range of concentration measured by this method is broader than the range covered by the reference method. The pre-mixed reagents incorporated in this method improve laboratory certainty in the performance of this method. Each reagent test is clearly labeled with the product number, so the analyst will not accidentally use the wrong reagent test, or label the cells incorrectly.

12.0 Data Analysis and Calculations The reference method defines calculations for the determination of the different types of chlorine (as stated above). The method indicates an MDL of 0.018 mg/L under optimum operating conditions. The ML is implied by the concentration range stated (0.05 – 5.0 mg/L). The method does not address significant digits.	**12.0 Data Analysis and Calculations** **Merck Spectroquant®-Type System Photometer** Results with a Merck Spectroquant® -type system photometer are displayed as chlorine concentration in mg /L. **Other Photometers** Measurement of samples with equivalent photometric equipment is accomplished by plotting absorbance against concentration of the calibration curve. This method defines the calculation for dilution factor correction in event that samples read outside the calibration range of the test. The Minimum Level (ML) for this method is 0.05 mg/L. If a result is obtained, which is lower than this ML, report the result as less than the ML (<0.05 mg/L). Report results to two significant digits.
13.0 Method Performance The method's performance data is referenced from another determinative technique for chlorine. There is a published study that contains performance data for all methods listed under SM 4500-Cl G.	**13.0 Method Performance** As in the SM 4500-Cl G reference method, this method incorporates similar chemical components, in the same proportions, and is determined similarly via photometric measurement. The precision and bias stated in the reference method are achievable by this method.
14.0 Pollution Prevention The reference method does not discuss pollution prevention.	**14.0 Pollution Prevention** The reagent tests, which are labeled as to the contents, and any potential dangers and health risks, have little chance of being disposed of incorrectly. The laboratory is reminded to properly manage these reagents in the laboratory to reduce any threat to the environment. General practices, such as ordering of supplies, can seriously impact the amount of materials, which require disposal in the laboratory. It is suggested that the laboratory only order supplies as demand dictates, to minimize expired materials requiring disposal.

15.0 Waste Management The reference method does not discuss waste management.	**15.0 Waste Management** Referenced in this section are two waste management documents for further information on this subject. The method does not specify restrictions for the chemicals used in this method. Instead, the laboratory is called upon to comply with all federal, state, and local regulations governing waste management.
16.0 References There are numerous journal articles listed throughout the reference method (general description and individual determinative techniques). This particular method lists eight journal or other publications in its bibliography section.	**16.0 References** This proposed method includes in the reference section, existing method documents for chlorine, supplemental and related documents for safety and general laboratory practices. Also included is the reference material, which outlines the instrument calibration procedures.
17.0 Tables The reference method includes a table in the calculation section. The table is used for guidance in calculating all types of chlorine from each of the determinations.	**17.0 Tables** **Table 1** This table summarizes the Spectroquant® Chlorine Cell Test comprised in this method. Included are concentration ranges and sample volumes required. **Table 2** This table outlines the procedure for preparing calibration curves solutions for the various concentration ranges covered by the Spectroquant® Chlorine Cell Tests. **Table 3** This table outlines the standardized performance acceptance criteria, for methods cited from 40 CFR Part 136, Table IB. This data must be achieved when the analyst initiates the method, attempts to prove initial demonstration of performance, and also ongoing performance of the method.
18.0 Glossary The reference method does not have a glossary.	**18.0 Glossary** See Section 3.0 The glossary defines terminology used in the body of method. Much of the terms defined are specific to the quality control section of the method. These terms are not used, or defined, in the reference method. This section clearly defines the nomenclature of the products being proposed for use.