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FREE CHLORINE DPD METHOD
Thermo Orion Method AC4P71

Revision 4, 7/9/02

Accepted by U.S. EPA on March 4, 2003 for drinking water compliance monitoring.

1.0   Scope and Applications

1.1   This method is a convenient packaging of the technology in "Standard Methods for the Analysis of Water and Wastewater" Method 4500 Cl G *(Ref.16.1)*. Method 4500 Cl G is an EPA-approved method for disinfectant compliance monitoring of drinking water. The present method is based on the use of Thermo Orion Cat. No. AC4P71, or equivalent test kit. It is used to determine residual free chlorine (See *Definitions, Section 3.1),* CAS Registry Number 7782-50-5.

1.2   The method is applicable to natural and treated waters at concentrations from 0.1-2.0 mg/L chlorine. Where sample results exceed the applicable range of the method, the sample must be diluted to within the applicable range and reanalyzed.

1.3   This method is for use in the Environmental Protection Agency's (EPA's) data gathering and monitoring programs under the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act.

1.4   The MDL for this method was determined to be 0.03 mg/L chlorine, using an AQUAfast AQ4000 Colorimeter and an AC4P71 Test Kit. This value was derived from the analysis of nine aliquots with a concentration of approximately 0.1 mg/L chlorine.

1.5   Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the quality control procedure in Section 9.2.

2.0   Summary of Method

Chlorine-containing samples are reacted with N, N-diethyl-p-phenylenediamine sulfate in the presence of a suitable buffer. The indicator and buffer are added in a combined powder form, and react with chlorine to produce a pink color. This compound is measured at 520 nanometers, using an LED-based spectrophotometer..

3.0 Definitions

3.1 Free Residual Chlorine—The amount of available chlorine present as aqueous molecular chlorine, hypochlorous acid, and hypochlorite ion. The ratio within these forms is pH- and temperature-dependent, and is not determined.

3.2 Material Safety Data Sheet (MSDS)- Written information provided for each chemical reagent or standard about a chemical's toxicity, health hazards, physical properties, flammability, and reactivity. It also includes storage, spill, and handling precautions.

3.3 Method Detection Limit (MDL)-The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.4 Calibration Blank (CB)- A volume of reagent water fortified with the same matrix as the calibration standard, but without the analytes, internal standards or surrogate analytes.

3.5 Calibration Standard (CAL)- A solution prepared from the primary dilution standard or stock standards and the internal standards and surrogate analytes. Used to calibrate the instrument response with respect to analyte concentration

3.6 Instrument Performance Check Solution (IPC)- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.7 Laboratory Fortified Blank (LFB)- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like the sample and is used to determine whether the methodology is in control, and if the laboratory is capable of making accurate and precise measurement.

3.8 Laboratory Reagent Blank (LRB)- An aliquot of reagent water or other blank matrices that are treated as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. Use the LRB to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

3.9 Quality Control Sample (QCS)- A solution of method analytes of known concentration that is used to fortify an aliquot of LRB or sample matrix. Obtain the QCS from a source external to the laboratory that is different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.10 <u>Matrix Spike (MS)</u>   An aliquot of an environmental sample, to which a known quantity of the method analyte is added in the laboratory. The MS is analyzed exactly like a environmental sample to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations.

3.11 <u>Matrix Spike Duplicate</u> (MSD) An aliquot of the same sample used for the MS, to which the exact same known quantity of the method analyte has been added as for the MS, and which is analyzed separately with the identical procedure. Analysis of the MS and MSD give a measure of the precision associated with the laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.12 <u>Calibration Range</u> The range of concentration of analyte for which the use of the method has been approved and for which the instrument has been pre-programmed with internal calibration, as given in the Method Scope, Section 1.

4.0   Interferences

4.1 Any oxidizing agents- these are usually present at insignificant concentrations compared to the residual chlorine concentrations.

4.2 Other disinfectants such as bromine, ozone, chlorine dioxide, peroxide, iodine and certain chloro-oxy disinfectant by-products may cause a positive interference in the DPD method.

4.3 Turbidity and sample color are normally compensated for during the "zeroing" step; if excessive turbidity is present, the instrument will indicate "overrng".

5.0   Safety

5.1 Use good laboratory practices throughout the test procedure. Follow the test procedure carefully and observe all precautionary measures.

5.2 An updated Material Safety Data Sheet (MSDS) is available for the reagents used in this method, which contains all known toxicological information.   Detailed information is available on the Internet, as well as by toll-free telephone. Go to www.thermo.com\waterapps and search on "AC4P71", or call 1-800-225-1480 or 1-978-232-6000.

5.3 When working with chlorine standards, if there is not adequate ventilation, it is appropriate to use a hood (when available).

5.4 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of all chemicals. Additional information on laboratory safety can be found in *Ref. 16.2.*

6.0   Equipment and Supplies

6.1   Chlorine Demand-Free Glassware

6.1.1   Treat all glassware used in sampling and testing to remove any chlorine demand. Soak all glassware with a dilute solution of chlorine bleach prepared by adding 1 mL commercial bleach to 1 liter of water. Allow to soak for at least one hour. After soaking, rinse the glassware thoroughly several times with DI water. Allow to dry before use.

6.2   Thermo Orion Cat. No. AC4P71 Free Chlorine Powder Chemistry Pack, or equivalent. .

6.3   Photometer, Thermo Orion AQ4000, or equivalent.

6.4   24 mm glass vials, Thermo Orion, Cat. No. AC2CUV, or equivalent.

6.5   Balance, capable of weighing to the nearest milligram, for preparing standards.

6.6   Volumetric flasks, 1 L, 100 mL.

6.7   Pipettes, 1 and 10 mL.

7.0   Reagents and Standards

7.1   Combined reagent tablet, Thermo Orion "DPD No. 4" , or equivalent.

7.2   Potassium Permanganate, ACS grade crystals.

7.3   Stock Potassium Permanganate Solution: Place 0.891 g $KMnO_4$ in a volumetric flask and dilute to 1 liter.

7.4   Standard Potassium Permanganate Solution: Dilute 10.00 mL of stock potassium permanganate solution (7.3 above) to 100 mL with distilled water in a volumetric flask. One mL of this solution diluted to 100 mL with distilled water is equivalent to 1.00 mg/L Chlorine.

8.0   Sample Collection and Storage

8.1   Chlorine in aqueous solution is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly. Exposure to sunlight or other strong light or agitation will accelerate the reduction of chlorine. Therefore, start chlorine determinations immediately after sampling.

8.2   Do not store samples.

8.3 Details on sampling techniques from conduits may be found in *Reference 16.3.*

9.0 Quality Control

9.1 Each laboratory using this method for compliance reporting is required to operate a formal quality control (QC) program *(see Reference 16.4).* The minimum requirements of this program are initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks, fortified samples, duplicates and other laboratory solutions as a continuing performance check. The laboratory must maintain performance records that define the quality of the data that are generated. See Section 17.1 for QC Performance Criteria.

9.2 Initial Demonstration Of Performance

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Calibration Range Verification - The calibration range must be verified at least every six months or whenever a significant change in instrument response is observed. The verification must use a minimum of a blank and three standards that cover the entire calibration range. Any verification data must verify that the instrument is within ±15% of calibration for each concentration used. If any verification data exceeds ±15% of calibration, recalibrate the instrument and repeat the procedure. If the problem is not resolved, call the kit manufacturer for assistance.

9.2.3 Quality Control Sample (QCS)- Obtain an independent quality control standard for total residual chlorine available from commercial sources (preferably verified against American Association for Laboratory Accreditation or National Institute of Standards and Technology reference materials, if available). If needed, dilute the standard according to the directions supplied with the standard to obtain standard concentrations within the linear calibration range.

When beginning the use of this method, on a quarterly basis, or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within 15% of the stated values, performance is unacceptable. Identify and correct the source of the problem before proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL)- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values (40 CFR, Part 136, Appendix B), take seven replicate aliquots of the

fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t \times S$$

Where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom]. S is the standard deviation of the replicate analyses. [t= 3.14 for seven replicates]

MDLs should be determined every six months, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

9.3   Assessing Laboratory Performance

9.3.1   Laboratory Reagent Blank (LRB)- The laboratory must analyze at least one LRB with each batch of samples. Perform a reagent blank determination according to Section 11.0, *Procedure,* substituting DI water for the sample. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination may be present and corrective actions must be taken before continuing the analysis.

9.3.2   Laboratory Fortified Blank (LFB)- The laboratory must analyze at least one LFB fortified with 1 mg/L total chlorine with each batch of samples. Calculate accuracy as percent recovery (see Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is out of control. Identify and resolve the problem before continuing analyses.

9.3.3   The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data are available (at least 20-30 analyses), the analyst may develop optional control limits from the percent mean recovery (x) and the single analyst standard deviation (S) of the mean recovery. Use these data to establish the upper and lower control limits as follows:

Upper Control Limit = x + 3S   Lower Control Limit = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%.

After each 5-10 new recovery measurements, calculate new control limits using only the most recent 20-30 data points. Also, use the standard deviation (S) data to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4   Instrument Performance Check Solution (IPC)

For all determinations the laboratory must analyze the IPC (a midrange check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required), and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ± 10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within + or – 10% .

If the calibration is not within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms the calibration is outside the limits, halt sample analysis, and determine the cause. In the case of drift, recalibrate the instrument, or contact the instrument manufacturer. Reanalyze all samples following the last acceptable IPC solution. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4   Assessing Analyte Recovery And Data Quality

9.4.1   Matrix Spike and Matrix Spike Duplicate (MS and MSD) *This is not applicable for samples containing excess reducing agents such as sulfur dioxide, or bisulfite.* The laboratory must add a known amount of analyte to an aliquot of at least 10% of the routine samples. The MS and MSD aliquots must be duplicates of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample level and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.2   Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated MS/MSD recovery range of 85-115%. In regulated monitoring, the percent relative range (RR) must be calculated using the following equation:

$$RR = 100 \frac{(|C_1 - C_2|)}{(C_1 + C_2)/2}$$

where:

C1= Concentration of the analyte in the MS sample, and
C1= Concentration of the analyte in the MSD sample.

The result obtained should be compared with the precision requirement listed in Section 17.1, "QC Performance Criteria".

9.4.3 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (see Section 9.3), the problem encountered with the LFM is matrix or solution related, not system related.

9.4.4 If reference materials are available, analyze them to provide additional performance data. Analyzing reference samples is valuable for demonstrating the ability to perform the method acceptably.

10.0 Calibration

10.1 General Precautions

10.1.1 Thoroughly clean vials, caps and stir rod after each analysis in order to prevent carry-over errors. Even minute reagent residues lead to incorrect measurements. Use the brush supplied with the kit for cleaning.

10.1.2 Ensure that the outer walls of the vials are dry and clean before performing the analysis. Fingerprints or water droplets on the light entry surfaces of the vials lead to incorrect measurements.

10.1.3 'Zero calibration' and 'Test Procedure' must be performed using the same vial, since different vials can possess slightly different tolerances.

10.1.4 For 'Zero calibration' and 'Test', ensure that the vial is always positioned in the sample chamber in such a way that the graduation with the white triangle points toward the same marking on the housing.

10.1.5 Always perform the zero calibration and the test procedure with capped vials.

10.1.6 Bubbles on the inside walls of the vial lead to incorrect measurements. To prevent this, cap the vial and remove the bubbles by swirling the vial before performing the test.

10.1.7 You must prevent water from penetrating into the sample chamber. The entry of water into the housing of the photometer can destroy electronic components and lead to corrosion damage.

10.1.8 Soiling of the lens (LED and photo sensor) in the sample chamber leads to incorrect measurements.

10.1.8.1 Check - and if necessary clean - the light entry surfaces of the sample chamber at regular intervals. Clean using a moist cloth and cotton balls.

10.1.9 Always add the reagent powders to the samples straight from the foil Do not touch powders with your fingers.

10.1.10 Major temperature differentials between the photometer and the environment can lead to incorrect measurements, due to the formation of condensate in the area of the lens or on the vial.

10.2 Zero Calibration

10.2.1. For best results, pipette samples, and zero using the sample, before each measurement. (The AQ4000, a multitest instrument, must be zeroed before each test method.)

10.2.2 Turn the colorimeter on by pressing the **power** key

10.2.3 Press **prgm** and select program **50** for the Free Chlorine measurement. Press **yes** key.

10.2.4 Fill a clean, dry 24 mm vial with 10 mL of sample

10.2.4 Screw the cap onto the vial and wipe the exterior of the vial to ensure it is clean and dry.

10.2.6. Insert the zero vial into the AQ4000 sample chamber. No adapters are required. Align the inverted triangle mark on the vial to the triangle mark on the colorimeter. Cover the vial with the vial cover.

10.2.7 Press the **zero** key. The "zero" icon will light up on the upper right hand corner.

10.2.8 "WAIT" is then displayed. The result is displayed as "0.000 A4P CL2 F" for free chlorine.

10.2.9. The colorimeter is now zeroed and ready for measurements.

11.0 Procedure

11.1 Using Program **50**, use the 24 mm vial with 10 mL of sample from the zero procedure.

11.2 Take one Chlorine Free DPD Powder Pack, tap down gently and tear open in the direction of the text. Add the contents to the sample vial.

11.3 Screw the cap onto the vial tightly and swirl vigorously to dissolve the powder. A pink color will develop if free chlorine is present.

11.4 Immediately, place the prepared sample into the AQ4000 sample chamber. Cover with the vial cover.

11.5 Press **meas** key for sample measurement.

11.6 The result, in mg/L free chlorine, will be shown on the instrument display.

11.7 If the display flashes "overrng", it is due to high chlorine levels. Dilute a fresh sample and repeat the test.   Multiply the result by the dilution factor. A slight loss of chlorine may occur during dilution.

12.0   Data Analysis and Calculations

12.1   The meter will read the results in mg/L chlorine.

12.2   Report results to the precision of three significant figures.

13.0   Method Performance

13.1   The method detection limit (MDL) study was performed by one analyst, and was determined to be 0.03 mg/L chlorine.

13.2   The minimum level (ML) for this method is 0.1 mg/L.

13.3   In a single laboratory, a single analyst performed replicate spiked sample analyses on a drinking water sample. The mean recovery for a 0.47 mg/L addition of free chlorine to a baseline drinking water sample containing 0.28 mg/L of free chlorine was 91.9%, with a relative standard deviation of 3.7% for n = 7 replicates.

14.0   Pollution Prevention

14.1   The small quantities of dye and buffers do not contribute significantly to pollution.

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 restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench

operations. Compliance with all sewage discharge permits and regulations is also required.

15.2   For further information on waste management, consult *Ref. 16.5*

16.0   References

16.1 "Standard Methods for the Examination of Water and Wastewater", 20th Edition, American Public Health Association, 1015 Fifteenth Street, NW, Washington, D.C. 20005, Method 4500-Cl G (1998).

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

16.3   "Standard Practices for Sampling Water," ASTM Annual Book of Standards, Part 31, D3370-76, American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

16.4   40 CFR part 136, Appendix A, Methods 1624 and 1625. See also, "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMS-CI, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

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16.5 "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.

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17.0   Tables and Validation Data

17.1   QC Performance Criteria

Type	Frequency	Acceptance Criteria
Laboratory Reagent Blank (LRB)	Daily	<0.05 mg/L chlorine
Precision (duplicates MS and MSD)	5-10%	RR equal to, or less than, 15% at 1 mg/L chlorine
Accuracy (LFB or MS/MSD)	5-10%	85-115 % recovery at 1 mg/L chlorine
Instrument Performance Check (IPC)	Immediately after any calibration; after every 10th sample and at the end of a sample run	90-110% of the initial calibration at 1 mg/L chlorine.
Independent Standard (QCS)	Initially, or quarterly, and as required to meet data quality needs	90-110% recovery at 1 mg/L chlorine.