METHOD #: 330.5	Approved for NPDES (Issued 1978)	
TITLE:	Chlorine, Total Residual (Spectrophotometric, DPD)	
ANALYTE:	CAS # Cl Chlorine 7782-50-5	
INSTRUMENTATION:	Spectrophotometer	
STORET No.	50060	

- 1.0 Scope and Application
 - 1.1 The DPD-Colorimetric method is applicable to natural and treated waters at concentrations from 0.2-4 mg/L.

2.0 Summary of Method

- 2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodide at pH 4 or less.
- 2.2 The liberated iodine reacts with N,N-diethyl-p-phenylene diamine (DPD) to produce a red colored solution.
- 2.3 The solution is spectrophotometrically compared to a series of standards, using a graph or a regression analysis calculation.
- 2.4 The results are read or calculated into mg/L Cl.

3.0 Interferences

- 3.1 Any oxidizing agents; these are usually present at insignificant concentrations compared to the residual chlorine concentrations.
- 3.2 Turbidity and color will essentially prevent the colorimetric analysis.

4.0 Apparatus

4.1 Spectrophotometer for use at 515 nm and cells of light path 1 cm or longer.

5.0 Reagents

- 5.1 Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na₂HPO₄, and 46 g anhydrous potassium dihydrogen phosphate, KH₂PO₄, in distilled water. Dissolve 800 mg disodium ethylenediamine tetraacetate dihydrate in 100 mL distilled water. Combine these two solutions and dilute to 1 liter with distilled water. Add 20 mg Hg Cl2 as a preservative.
- 5.2 N,N-Diethyl-p-phenylenediamine (DPD) indicator solution: Dissolve 1 g DPD oxalate or 1.5 g p-amino-N,N-diethylaniline sulfate in chlorine free distilled water containing 8 mL of 1+3 H₂SO₄(5.3) and 200 mg disodium ethylenediamine tetraacetate dihydrate. Dilute to 1 liter, store in a colored, glass-stoppered bottle. Discard when discolored. The buffer and indicator

sulfate are available as a combined reagent in stable powder form. CAUTION: The oxalate is toxic, avoid ingestion.

- 5.3 Sulfuric acid solution (1 + 3): Slowly add one part of H₂SO₄(sp. gr. 1.84) to three parts of distilled water.
- 5.4 Potassium Iodide, KI crystals.
- 5.5 Stock Potassium Permanganate Solution: Place 0.891 g KMnO₄ in a volumetric flask and dilute to 1 liter.
- 5.6 Standard Potassium Permanganate Solution: Dilute 10.00 mL of stock potassium permanganate solution (5.5) to 100 mL with distilled water in a volumetric flask. One milliliter of this solution diluted to 100 mL with distilled water is equivalent to 1.00 mg/L Cl.
- 6.0 Procedure
 - 6.1 Calibration
 - 6.1.1 Prepare a series of permanganate standards covering the chlorine equivalent range of 0.05 to 4 mg/L.
 - 6.1.2 Place 5 mL phosphate buffer (5.1) in a flask.
 - 6.1.3 Add 5 mL DPD reagent (5.2).
 - 6.1.4 Add 100 mL permanganate standard (6.1.1).
 - 6.1.5 Read at 515 nm on a spectrophotometer and record the absorbance.
 - 6.1.6 Return the contents of the cell to the flask.
 - 6.1.7 Titrate the contents of the flask with standard ferrous ammonium sulfate (DPD- FAS Method), until the red color is discharged. Record the result.
 - 6.2 Sample Analysis
 - 6.2.1 Place 0.5 mL phosphate buffer (5.1) in flask.
 - 6.2.2 Add 0.5 mL DPD reagent (5.2).
 - 6.2.3 Add approximately 0.1 g KI (5.4).
 - 6.2.4 Add 10 mL of sample.
 - 6.2.5 Let stand 2 minutes.
 - 6.2.6 Read at 515 nm on a spectrophotometer, and record the absorbance.
- 7.0 Calculations
 - 7.1 Calibration Curve Method
 - 7.1.1 Plot the absorbance of the standard permanganate solutions (6.1.5) on the vertical axis versus the titrated concentration (6.1.7) on the horizontal axis.
 - 7.1.2 Draw the line of best fit through the points.
 - 7.1.3 Locate the absorbance (6.2.6) of the sample on the vertical axis.
 - 7.1.4 Read the concentration on the horizontal axis at the intersect of the absorbance and the calibration line.
 - 7.2 Regression Analysis Calculation-Computerized
 - 7.2.1 Enter the absorbance data of the standard permanganate solutions (6.1.5) and the respective titrated concentrations (6.1.7) in the appropriate places in the program.
 - 7.2.2 Enter the absorbance data of the sample.
 - 7.2.3 The computer will then display the concentration in mg/L Cl.

8.0 Precision and Accuracy

8.1 Twenty-five laboratories analyzed prepared samples of 0.66 mg/L Cl. The relative standard deviation was 27.6% and the relative error was 15.6%. In a single laboratory, single operator situation the following results were obtained.

Sample	Average	Std. Dev	Rel. Std. Dev.Matrix	
	mg/L	± mg/L	%	
Distilled Water(a)	0.39	0.012	3.1	
	3.61	0.11	3.2	
Drinking Water	0.94	0.008	0.8	
River Water	0.86	0.02	1.9	
Domestic Sewage	1.07	0.03	2.4	

(a) Three replicates for distilled water. Seven replicates for other samples.

For three samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Sample	Iodometric	DPD	% Recovery
Matrix	Titration	Colorime-	-
	mg/L	tric mg/L	
Drinking Water	0.86	0.94	109.3
River Water	0.70	0.86	122.9
Domestic Sewage	1.01	1.07	106.0

Bibliography

- 1. Standard Methods for the Examination of Water and Wastewater, 14th Ed., Pg. 332, Method 409F, "DPD Colorimetric Method", (1975).
- 2. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4-78-019.