CHLORINE, TOTAL RESIDUAL

Method 330.4 (Titrimetric, DPD-FAS)

STORET NO. 50060

1. Scope and Application
   1.1 The N,N-diethyl-p-phenylene diamine (DPD) – ferrous ammonium sulfate (FAS) titration method is applicable to natural and treated waters at concentrations above 0.1 mg/l Cl.
2. 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 iodine is titrated with FAS using DPD as the indicator.
   2.3 The results are calculated as mg/l Cl even though the actual measurement is of total oxidizing power because chlorine is the dominant oxidizing agent present.
3. Interferences
   3.1 Bromine, bromamine and iodine are interferences which are normally present in insignificant amounts.
   3.2 Oxidized manganese interferes but can be corrected by subtraction after performing a titration in the presence of sodium arsenite ($NaAsO_2$)
   3.3 Copper interferes but is accounted for (up to approximately 10 mg/l copper) by incorporation of EDTA. The EDTA also retards deterioration of DPD due to oxidation and completely suppresses dissolved oxygen errors by preventing trace metal catalysis.
   3.4 Turbidity and color may make the endpoint difficult to detect. Practice runs with spiked samples may be necessary.
4. Apparatus
   4.1 Standard laboratory glassware is used. A microburet, 0–2 ml or 0–10 ml, depending on the concentration range expected, is used.
5. Reagents
   5.1 Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, 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. $HgCl_2$ 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 H_2SO_4 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.

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5.3 Standard ferrous ammonium sulfate (FAS) titrant: Dissolve 1.106g Mohr's salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in distilled water containing 1 ml of 1 + 3 H_2SO_4 (5.4) and make up to 1 liter with freshly boiled and cooled distilled water. Stable for one month. Check with titration by standard potassium dichomate (5.5). The FAS titrant is equivalent to 100 ug Cl/1.00 ml.

5.4 Sulfuric acid solution (1+3): Slowly add one part of H_2SO_4 (sp. gr. 1.84) to three parts of distilled water.

5.5 Potassium dichromate (0.1000N): Dissolve 4.904 g potassium dichromate ($K_2Cr_2O_7$) in distilled water and dilute to 1 liter.

5.6 Potassium Iodide, KI Crystals.

5.7 Sodium Arsenite Solution: Place 500 mg of sodium arsenite ($NaAsO_2$) in a flask and dilute to 100 ml with distilled water.

6. Procedure

6.1 This procedure gives a convenient direct reading (ml titrant = mg/1 Cl) up to 4 mg/1. An aliquot should be diluted to 100 ml if higher concentrations are present.

6.2 Place 5 ml of phosphate buffer (5.1) in a titration flask.

6.3 Add 5 ml of DPD indicator (5.2).

6.4 Add approximately 1 g of KI (5.6) on a scoop.

6.5 Add 100 ml of sample.

6.6 Wait 2 minutes.

6.7 Titrate with FAS (5.3) until the red color is discharged. Record the volume of titrant used.

6.8 If oxidized manganese is present

6.8.1 Place 5 ml of phosphate buffer (5.1) in a titration flask.

6.8.2 Add one small crystal of potassium iodide (5.6).

6.8.3 Add 0.5 ml of sodium arsenite solution (5.7).

6.8.4 Add 100 ml of sample. Mix.

6.8.5 Add 5 ml DPD indicator (5.2). Mix.

6.8.6 Titrate wth FAS (5.3) until the red color is discharged. Record the volume of titrant used.

7. Calculations

7.1 The ml of FAS titrant is equal to the mg/1 Cl. If oxidized manganese was present, subtract the amount of titrant used in 6.8.6 from the amount of titrant used in 6.7 to obtain the mg/1 Cl.

8. Precision and Accuracy

Nineteen laboratories analyzed prepared samples of 0.64 and 1.83 mg/1 Cl. The relative standard deviations were 19.2 and 9.4% respectively and the relative errors were 8.1 and 4.3% respectively.

In a single operator single laboratory situation the following results were obtained.

Sample Matrix	Average mg/l	Stand. Dev ±mg/l	Rel. Stnd. Dev %
Distilled Water[a]	0.34	0.02	5.6
	0.65	0.003	0.5
	3.45	0.02	0.5
Drinking Water	0.98	0.01	1.2
River Water	0.79	0.01	1.4
Domestic Sewage	1.08	0.02	1.8
Raw Sewage	0.79	0.03	3.3

[a]Three replicates for distilled water. Seven replicates for other samples.

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

Sample Matrix	Iodometric Titration mg/l	DPD FAS Titration mg/l	% Recovery
Drinking Water	0.91	0.98	107.7
River Water	0.73	0.79	108.2
Domestic Sewage	1.20	1.08	90.0
Raw Sewage	0.75	0.79	105.3

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Ed. Page 329, Method 409E, "DPD Ferrous Titrimetic 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.

CHLORINE, TOTAL RESIDUAL

Method 330.5 (Spectrophotometric, DPD)

STORET NO. 50060

1. Scope and Application
   1.1 The DPD-Colorimetric method is applicable to natural and treated waters at concentrations from 0.2–4 mg/1.
2. 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/1 Cl.
3. 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. Apparatus
   4.1 Spectrophotometer for use at 515 nm and cells of light path 1 cm or longer.
5. Reagents
   5.1 Phosphate buffer solution: Dissolve 24 g anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, 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 $HgCl_2$ 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 H_2SO_4 (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 H_2SO_4 (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 $KMnO_4$ in a volumetric flask and dilute to 1 liter.

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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/1 Cl.

6. Procedure

6.1 Calibration

6.1.1 Prepare a series of permanganate standards covering the chlorine equivalent range of 0.05 to 4 mg/1.

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. 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/1 Cl.

8. Precision and Accuracy

Twenty-five laboratories analyzed prepared samples of 0.66 mg/1 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 Matrix	Average mg/l	Stnd. Dev.[a] ±mg/l	Rel. Stnd. Dev.[a] %
Distilled Water	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 Matrix	Iodometric Titration mg/l	DPD Colorimetric mg/l	% Recovery
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.