

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.
- 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 mg/L	Std. Dev ± mg/L	Rel. Std. Dev. Matrix %
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 Matrix	Iodometric Titration mg/L	DPD Colorime- tric 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.