METHOD #: 330.3 Approved for NPDES (Issued 1978)

TITLE: Chlorine, Total Residual (Titrimetric, Iodometric)

ANALYTE: CAS # Cl2 Chlorine 7782-50-5

INSTRUMENTATION: Titration

STORET No. 50060

1.0 Scope and Application

1.1 The iodometric titration method is applicable to natural and treated waters at concentrations greater than 0.1 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 iodine is titrated with a standard reducing agent such as sodium thiosulfate or phenylarsine oxide using a starch 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.

3.0 Interferences

3.1 Ferric, manganic and nitrite ions interfere, the neutral titration minimizes these interferences.
3.2 Acetic acid is used for the acid titration. Sulfuric acid may be used if no interferences are present. Hydrochloric acid should never be used.
3.3 Turbidity and color may make the endpoint difficult to detect. Practice runs with spiked samples may be necessary.

4.0 Apparatus

4.1 Standard laboratory glassware is used. A microburet 0-2 mL or 0-10 mL is used depending on the desired range and accuracy.

5.0 Reagents

5.1 Acetic acid, conc (glacial)
5.2 Potassium iodide, KI, crystals
5.3 Phenylarsine oxide (0.00564N): Wallace and Tiernan or equivalent. Standardize with potassium biiodate (5.8, 5.12).
5.4 Phenylarsine oxide (0.0375N): Hach Chemical Co. or equivalent. Standardize with potassium biiodate (5.7, 5.13).
5.5 Commercially available starch indicators such as thyodene or equivalent may

be used.

5.6 Potassium biiodate (O.lN): Dissolve 3.249 g potassium biiodate, previously dried two hours at 103°C, in distilled water and dilute to 1.0 liter. Store in a glass stoppered bottle.

5.7 Potassium biiodate (0.05N): Dilute 500 mL of 0.1 N potassium biiodate (5.6) to 1 liter in a volumetric flask. Store in glass stoppered bottle.

5.8 Potassium biiodate (0.005N): Dilute 50 mL of 0.1 N potassium biiodate (5.6) to 1 liter in a volumetric flask. Store in glass stoppered bottle.

5.9 Standard iodine solution (O.1N): Dissolve 40 g KI in 25 mL distilled water, add 13 g resublimed iodine and stir until dissolved. Transfer to a 1 liter volumetric flask and dilute to the mark. Determine the exact normality (5.14).

5.10 Standard iodine titrant (0.0282N): Dissolve 25 g-KI in a little distilled water in a 1 liter volumetric flask. Add the calculated amount of 0.1 N standard iodine to produce a 0.0282 N solution. Standardize daily (5.15). Store in amber bottle or in dark; protect from sunlight at all times and keep from contact with rubber.

5.11 Sulfuric acid solution (1:4): Slowly add 200 mL H_2SO_4 (sp. gr. 1.84) to 800 mL of distilled water.

5.12 Standardization of 0.00564N phenylarsine oxide: Dissolve approximately 2 g (± 1 g) KI (5.2) in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (5.11) followed by 20 mL 0.005 N potassium biiodate solution (5.8). Place in dark for 5 minutes, dilute to 300 mL and titrate with 0.00564N phenylarsine oxide solution (5.3) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determination should agree within ± 0.05 mL.

$$NPAO = \frac{20 \times 0.005}{ml\ PAO}$$

Adjust PAO solution if necessary and recheck.

5.13 Standardization of 0.037SN phenylarsine oxide: Dissolve approximately 2 g (±1 g) KI (5.2) in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (5.11) followed by 20 mL 0.05 N potassium biiodate solution (5.7). Place in dark for 5 minutes, dilute to 300 mL and titrate with 0.0375 N phenylarsine oxide solution (5.4) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 mL.

$$NPAO = \frac{20 \times 0.1}{ml\ PAO}$$

Adjust PAO solution if necessary and recheck.

5.14 Standardization of 0.1 N iodine solution: Dissolve approximately 2 g (± 1 g) KI (5.2) in 100 to 150 mL distilled water; add 20 mL iodine solution (5.9). Dilute to 300 mL and titrate with 0.0375 N phenylarsine oxide solution (5.4) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±O.05 mL.

$$N_{I_2} = \frac{mL\ PAO \times 0.0375}{20}$$

Adjust iodine solution if necessary and recheck.

5.15 Standardization of 0.0282N iodine solution: Dissolve approximately 2 g (±1 g) KI (5.2) in 100 to 150 mL distilled water; add 20 mL iodine solution (5.10). Dilute to 300 mL and titrate with 0.0375 N phenylarsine oxide solution (5.4) to a pale straw color. Add a small scoop of indicator (5.5). Wait until homogeneous blue color develops and continue the titration drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 mL.

$$N_{I_2} = \frac{mL\ PAO \times 0.0375}{20}$$

Adjust iodine solution if necessary and recheck.

6.0 Procedure

6.1 This procedure gives a convenient direct reading (mL titrant = mg/L Cl) in the range of the microburet (0.5 mL to 2,5 or 10 ml). The sample volume and reagent normalities may be varied at the analyst's discretion.

6.2 Place 5 mL acetic acid in an Erlenmeyer flask containing a Teflon coated magnetic stirring bar.

6.3 Add about 1 g KI (5.2) estimated on a spatula.

6.4 Add 200 mL sample.

6.5 Place on magnetic stirrer under buret.

6.6 Titrate away from direct sunlight with 0.00564N PAO (5.3) to a pale straw color. Add a scoop of indicator (5.5). Wait until blue color is homogeneously distributed, continue titrating until blue color is discharged. The mL of PAO is equal to the mg/L Cl plus or minus the blank correction (6.7) if any.

6.7 Blank titration: Using distilled water in place of the sample perform steps 6.2-6.5, add a scoop of indicator. Perform either 6.7.1 or 6.7.2 depending on color development.

6.7.1 Blank titration A: If a blue color develops titrate with 0.00564N PAO (5.3) to the disappearance of the blue color and record the results.

6.7.2 Blank titration B: If no blue color develops titrate with 0.0282N iodine (5.10) until blue color appears. Back titrate with 0.00564N PAO (5.3) and record the difference as titration B.

7.0 Calculations

7.1 The mL of PAO titrant is equal to mg/L Cl under the volumes and concentrations described. The blank correction A (6.7.1) can be directly subtracted. The blank correction B (6.7.2), which is added, involves a factor of 5 (unless one substitutes 0.00564N iodine for the 0.0282N iodine). Normally the reagents are pure enough that the blank correction is insignificant and therefore unnecessary.

8.0 Precision and Accuracy

8.1 Thirty to thirty two laboratories analyzed prepared samples of 0.64, 0.84 and 1.83 mg/L. The relative standard deviations were 27.0%, 32.4% and 23.6% respectively and relative errors were 23.6%, 18.5%, and 16.7% respectively. In a single operator, single laboratory, situation the following results were obtained.

Sample matrix	Average mg/L	Standard deviation ±mg/L	Rel. standard deviation %
Distilled Water(a)	0.25	0.001	0.23
	4.02	0.03	0.76
Drinking Water	0.68	0.04	5.2
River water	0.30	0.03	9.7
Domestic Sewage(b)	1.11	0.06	5.9
Raw sewage	0.48	0.09	18.0

(a) Three replicates for distilled water. Seven replicates for other sample matrices.
(b) Secondary treatment

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th ed. p. 316, Method 409A "Iodometric Method I" (1975).
2. ASTM Standards, Part 31, "Water", p. 276, Method D1253-76(1976).
3. Bender, D. F., "Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices", EPA Report-600/4-78-019.