METHOD #: 330.2	Approved for NPDES (Issued 1978)
TITLE:	Chlorine, Total Residual (Titrimetric, Back, Iodometric (Starch or Amperometric)
ANALYTE:	CAS # Cl Chlorine 7782-50-5
INSTRUMENTATION:	Titration
STORET No.	50060

1.0 Scope and Application

1.1 The iodometric back titration method is applicable to all types of waters but is primarily used for wastewater because it eliminates any contact between the full concentration of liberated iodine and the wastewater.

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 immediately quantitatively oxidizes a standardized reducing agent such as sodium thiosulfate or phenylarsine oxide.
2.3 The excess reducing agent is then determined by titrating with a standard iodine titrant. The starch endpoint color change is from clear to blue.
2.4 A subtraction of the excess amount of reducing agent is included in the calculations and the results are reported 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 Manganese, iron and nitrite interference may be minimized by buffering to pH 4 before the addition of KI.
3.2 High concentrations of organics may cause uncertainty in the endpoint. This uncertainty can be reduced by acidifying to pH 1.0 if manganese, iron and nitrite are absent.
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 Phenylarsine oxide solution (0.00564N): Wallace and Tierman or equivalent.

Standardize with potassium biiodate (5.6, 5.9).

5.2 Acetate buffer solution (pH 4): Dissolve 146 g anhydrous $NaC_2H_3O_2$ or 243 g $NaC_2H_3O_2*3H_2O$ in 400 mL distilled water, add 480 g conc acetic acid and dilute to 1 liter with distilled water.

5.3 Standard iodine solution (O.IN): 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 (5.11).

5.4 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 (5.3) to produce a 0.0282N solution. Standardize daily (5.12). Store in amber bottle or in dark; protect from sunlight at all times and keep from contact with rubber.

5.5 Potassium biiodate (O.1N): Dissolve 3.249g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Store in a glass stoppered bottle.

5.6 Potassium biiodate (0.005N): Dilute 50 mL of 0.1N potassium biiodate (5.5) to 1 liter in a volumetric flask. Store in glass stoppered bottle.

5.7 Commercially available starch indicators such as thyodene or equivalent may be used.

5.8 Sulfuric Acid Solution (1:4): Slowly add 200 mL H_2SO_4 (sp. gr. 1.84) to 800 mL of distilled water.

5.9 Standardization of 0.00564N phenylarsine oxide: Dissolve approximately 2g (± 1g) KI in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (5.8) followed by 20 mL 0.005N potassium biiodate solution (5.6). Place in dark for 5 minutes; dilute to 300 mL and titrate with 0.00564N phenylarsine oxide solution (5.1) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous 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.

$$\text{NPAO} = \frac{20 \times 0.005}{\text{mL PAO}}$$

Adjust PAO solution if necessary and recheck.

5.10 Standardization of 0.037SN phenylarsine oxide: Dissolve approximately 2 g (± 1g) KI in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (5.8) followed by 20 mL O.1N potassium biiodate solution (5.5). Place in dark for 5 minutes, dilute to 300 mL and titrate with 0.0375N phenylarsine oxide solution (5.10) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous 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.

$$\text{NPAO} = \frac{20 \times 0.005}{\text{mL PAO}}$$

Adjust PAO solution if necessary and recheck.

5.11 Standardization of 0.1N Iodine solution: Dissolve approximately 2g (± 1 g) KI in 100 to 150 mL distilled water; add 20 mL Iodine Solution (5.3). Dilute to 300 mL and titrate with 0.037SN phenylarsine oxide solution (5.10) to a pale straw

color. Add a small scoop of indicator (5.7). Wait until homogenous blue color develops and continue the titration 330.2-2 drop by drop until the color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 mL.

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

Adjust iodine solution if necessary and recheck.

5.12 Standardization of 0.0282N Iodine solution: Dissolve approximately 2 g (± 1.g) KI in 100 to 150 mL distilled water; add 20 mL Iodine solution (5.4). Dilute to 300 mL and titrate with 0.0375N phenylarsine oxide solution (5.10) to a pale straw color. Add a small scoop of indicator (5.7). Wait until homogenous 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.

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

Adjust iodine solution if necessary and recheck.

6.0 Procedure

6.1 Starch-Iodide End Point

6.1.1 Place 5.00 mL of 0.00564N PAO solution (5.9) in a flask.

6.1.2 Add approximately 1g KI on a scoop.

6.1.3 Add 4 mL acetate buffer solution (5.2).

6.1.4 Add 200 mL of sample. For concentrations above 10 mg/L, a sample of less volume may be diluted to 200 mL with chlorine-free, chlorine demand-free distilled water.

6.1.5 Mix well.

6.1.6 Add approximately 4 mg indicator (5.7) just before titration.

6.1.7 Titrate with 0.0282N iodine solution (5.12) to the first appearance of a blue color that persists after mixing. Record the mL of titrant used.

6.2 Amperometric End Point

6.2.1 Perform steps 6.1.1-6.1.5 inclusive or follow the directions of the manufacturer of the amperometric titrator. Prepackaged reagents should be checked (restandardized).

6.2.2 Place the solution in the proper position on the amperometric titrater.

6.2.3 Titrate with 0.0282N Iodine Solution (5.12) Observe the response of the meter needle. Initially the needle will remain stationary. As the endpoint is approached the needle will temporarily deflect, then return to or near to its original position. Continue dropwise. When the needle deflects and remains deflected the end point has been exceeded by one drop. Subtract 1/20th of an mL from the buret reading and record the result.

7.0 Calculations

$$\text{mg/L Cl} = \frac{(A - 5B) \times 200}{C}$$

where:

A = mL 0.00564 N PAO
B = mL 0.0282 N I_2
C = mL sample

8.0 Precision and Accuracy

8.1 Starch-Iodine Endpoint

8.1.1 Precision

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

Sample Matrix	Average mg/L	Stand. Dev. ±mg/L	Rel. Stand. Dev. %
Distilled Water(a)	0.41	0.05	12.2
	3.51	0.12	3.3
Drinking Water	0.84	0.04	4.3
River Water	0.84	0.02	2.7
Domestic Sewage(b)	0.87	0.07	7.6
Raw Sewage	0.55	0.09	16.0

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

8.1.2 Accuracy(Relative)

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

Iodometric Sample Matrix	Starch Titration mg/L	Iodide Back Titration mg/L	% Recovery
Drinking Water	0.85	0.84	98.8
River Water	0.78	0.84	107.7
Domestic Sewage	1.00	0.87	87.0
Raw Sewage	Approx 0.5	0.55	Approx 100.0

8.2 Amperometric End Point

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

Sample Matrix	Average mg/L	Stand. Dev. ± mg/L	Rel. Stand. Dev. %
Distilled Water(a)	0.58	0.05	8.8
	3.53	0.07	2.0
Drinking Water	0.82	0.05	5.9
River Water	0.68	0.06	9.4
Domestic Sewage(b)	1.10	0.09	8.3

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

8.2.2 Accuracy

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	Amperometric Back Titration mg/L	% Recovery
Drinking Water	0.83	0.82	98.8
River Water	0.66	0.68	103.0
Domestic Sewage	1.45	1.10	75.7

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Ed., p. 318, Method 409B "Iodometric Method II", (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.