

- 5.2 Potassium Iodide, KI, crystals.
- 5.3 Potassium Iodide Solution: Dissolve 50 g KI in freshly boiled and cooled distilled water and dilute to 1 liter. Store in colored, glass-stoppered bottle in refrigerator. Discard when yellow color develops.
- 5.4 Commercially available starch indicators such as thyodene or equivalent may be used.
- 5.5 Acetate buffer solution (pH 4): Dissolve 146g anhydrous $\text{NaC}_2\text{H}_3\text{O}_2$ or 243g $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 400 mL distilled water, add 480g conc acetic acid and dilute to 1 liter with distilled water.
- 5.6 Sulfuric Acid (1:4): Slowly add 200 mL H_2SO_4 (sp. gr. 1.84) to 800 mL of distilled water.
- 5.7 Potassium biiodate (0.1N): Dissolve 3.249g potassium biiodate, previously dried 2 hours at 103°C , in distilled water and dilute to 1.0 liters. Store in a glass stoppered bottle.
- 5.8 Potassium biiodate (0.005N): Dilute 50 mL of 0.1 N potassium biiodate (5.7) to 1-liter in a volumetric flask. Store in a glass stoppered bottle.
- 5.9 Standardization of 0.00564N phenylarsine oxide: Dissolve approximately 2g (\pm 1g) KI (5.2) in 100 to 150 mL distilled water; add 10 mL H_2SO_4 solution (5.6) followed by 20 mL 0.005N potassium biiodate solution (5.8). 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 (5.4). 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.

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

Adjust PAO solution if necessary and recheck.

6.0 Procedure

- 6.1 Place 200 mL of sample in the sample container. This volume is convenient because the buret reading in milliliters is equivalent to mg/L Cl. Up to 2 mg/L is reliably titrated this way. Smaller sample aliquots diluted to 200 mL are used for concentrations greater than 2 mg/L. The construction of the cell and electrode component usually require 200 mL of sample.
- 6.2 Place on electrode assembly.
- 6.3 Add 1.0 mL KI solution (5.3).
- 6.4 Add 1 mL acetate buffer (5.5).
- 6.5 Titrate with 0.00564N PAO (5.1).
- 6.6 As each increment is added the needle deflects toward rest. When the needle no longer deflects subtract the last drop added from the buret reading to obtain the mg/L Cl. Less and/or slower deflection signals that the end point is near.

7.0 Calculations

- 7.1 For 0.00564N PAO and a 200 mL sample there are no calculations. The buret reading is in mg/L. The last increment, when the needle does not deflect toward rest, must be subtracted.

8.0 Precision and Accuracy

- 8.1 More than 20 laboratories analyzed prepared samples of 0.64 and 1.83mg/L total Cl. The relative standard deviations were 24.8% and 12.5% respectively and the relative errors were 8.5% and 8.8% respectively.

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	0.38	0.02	6.1
	3.50	0.01	0.2
Drinking Water	0.97	0.03	2.6
River Water	0.57	0.02	3.0
Domestic Sewage	0.41	0.03	6.9

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

Sample Matrix	Iodometric Titration mg/L	Amperometric Titration mg/L	% Recovery
Drinking Water	0.94	0.97	103.2
River Water	0.56	0.57	101.8
Domestic Sewage	0.50	0.41	82.0

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 322, Method 409C (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1253-76, p 277, Method A (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.