

# IODIDE

## Method 345.1 (Titrimetric)

STORET NO. 71865

1. Scope and Application
  - 1.1 This method is applicable to drinking, surface and saline waters, sewage and industrial waste effluents.
  - 1.2 The concentration range for this method is 2–20 mg/1 of iodide.
2. Summary of Method
  - 2.1 After pretreatment to remove interferences, the sample is analyzed for iodide by converting the iodide to iodate with bromine water and titrating with phenylarsine oxide (PAO) or sodium thiosulfate.
3. Sample Handling and Preservation
  - 3.1 Store at 4°C and analyze as soon as possible.
4. Interferences
  - 4.1 Iron, manganese and organic matter can interfere; however, the calcium oxide pretreatment removes or reduces these to insignificant concentrations.
  - 4.2 Color interferes with the observation of indicator and bromine-water color changes. This interference is eliminated by the use of a pH meter instead of a pH indicator and the use of standardized amounts of bromine water and sodium formate solution instead of observing the light yellow color changes.
5. Reagents
  - 5.1 Acetic Acid Solution (1:8): Mix 100 ml of glacial acetic acid with 800 ml of distilled water.
  - 5.2 Bromine Water: In a fume hood, add 0.2 ml bromine to 500 ml distilled water. Stir with a magnetic stirrer and a Teflon-coated stirring bar for several hours or until the bromine dissolves. Store in a glass-stoppered colored bottle.
  - 5.3 Calcium Oxide (CaO): Anhydrous, powdered.
  - 5.4 Potassium Iodide (KI): Crystals, ACS Reagent Grade.
  - 5.5 Sodium Acetate Solution (275 g/1): Dissolve 275 g of sodium acetate trihydrate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ) in distilled water. Dilute to 1 liter and filter.
  - 5.6 Sodium Formate Solution (500 g/1): Dissolve 50 g of sodium formate ( $\text{NaCHO}_2$ ) in hot distilled water and dilute to 100 ml.
  - 5.7 Nitrogen Gas: Cylinder.
  - 5.8 Sulfuric Acid Solution (1:4): Slowly add 200 ml of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to 800 ml of distilled water.
  - 5.9 Phenylarsine Oxide (0.0375 N): Hach Chemical Co. or equivalent. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).

Issued 1974

- 5.10 Phenylarsine Oxide Working Standard (0.0075 N): Transfer 100 ml of commercially available 0.0375 N phenylarsine oxide (5.9) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.
- 5.11 Commercially available starch indicators such as thyodene or equivalent may be used.
- 5.12 Sodium Thiosulfate, Stock Solution, 0.75 N: Dissolve 186.15 g ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in boiled and cooled distilled water and dilute to 1.0 liter. Preserve by adding 5 ml chloroform.
- 5.13 Sodium Thiosulfate Standard Titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1.0 liter. Preserve by adding 5 ml of chloroform. Standardize with 0.0375 N potassium biiodate (5.15, 5.18).
- 5.14 Sodium Thiosulfate Working Standard (0.0075 N): Transfer 100 ml of sodium thiosulfate standard titrant (5.13) to a 500 ml volumetric flask and dilute to the mark with distilled water. This solution should be prepared fresh daily.
- 5.15 Potassium Biiodate Standard, 0.0375 N: Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in distilled water and dilute to 1.0 liter. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.
- 5.16 Starch Solution: Prepare an emulsion of 10 g of soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator. Commercially available, powdered starch indicators may be used in place of starch solution.
- 5.17 Potassium Fluoride ( $\text{KF} \cdot 2\text{H}_2\text{O}$ ): ACS Reagent Grade
- 5.18 Standardization of 0.0375 N Phenylarsine Oxide and 0.0375 N sodium thiosulfate: Dissolve approximately 2 g ( $\pm 1.0$  g) KI (5.4) in 100 to 150 ml distilled water; add 10 ml  $\text{H}_2\text{SO}_4$  solution (5.8) followed by 20 ml standard potassium biiodate solution (5.15). Place in dark for 5 minutes, dilute to 300 ml and titrate with phenylarsine oxide (5.9) or sodium thiosulfate standard titrant (5.13) to a pale straw color. Add a small scoop of indicator (5.11). Wait until homogeneous color develops and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within  $\pm 0.05$  ml.

## 6. Procedure

### 6.1 Pretreatment

- 6.1.1 Add a visible excess of CaO (5.3) to 400 ml of sample. Stir or shake vigorously for approximately 5 minutes. Filter through a dry, moderately retentive filter paper, discarding the first 75 ml.

### 6.2 Iodide Determination

- 6.2.1 Place 100 ml of pretreated sample (6.1) or a fraction thereof diluted to that volume, into a 150 ml beaker. Add a Teflon-coated stirring bar and place on a magnetic stirrer. Insert a pH electrode and adjust the pH to approximately 7 or slightly less by the dropwise addition of  $\text{H}_2\text{SO}_4$  solution (5.8).
- 6.2.2 Transfer the sample to a 250 ml wide-mouthed conical flask. Wash beaker with small amounts of distilled water and add washings to the flask.

**NOTE:** A 250 ml iodine flask would increase accuracy and precision by preventing possible loss of the iodine generated upon addition of potassium iodide and sulfuric acid (6.3.1).

- 6.2.3 Add 15 ml sodium acetate solution (5.5) and 5 ml acetic acid solution (5.1). Mix well. Add 40 ml bromine water solution (5.2); mix well. Wait 5 minutes.
  - 6.2.4 Add 2 ml sodium formate solution (5.6); mix well. Wait 5 minutes.
  - 6.2.5 Purge the space above the sample with a gentle stream of nitrogen (5.7) for approximately 30 seconds to remove bromine fumes.
  - 6.2.6 If a precipitate forms (iron), add 0.5 g  $\text{KF} \cdot 2\text{H}_2\text{O}$  (5.17).
  - 6.2.7 A distilled water blank must be run with each set of samples because of iodide in reagents. If a blank is consistently shown to be zero for a particular "lot" of chemicals it can then be ignored.
- 6.3 Titration
- 6.3.1 Dissolve approximately 1 g potassium iodide (5.4) in sample. Add 10 ml of  $\text{H}_2\text{SO}_4$  solution (5.8) and place in dark for 5 minutes.
  - 6.3.2 Titrate with phenylarsine oxide working standard (5.10) or sodium thiosulfate working standard solution (5.14) adding indicator (5.11 or 5.15) as end point is approached (light straw color). Titrate to colorless solution. Disregard returning blue color.
7. Calculations

$$\text{I}^-(\text{mg/l}) = 21,150 \left( \frac{\text{ml} \times \text{N}}{\text{V}} \right)$$

where:

ml = the number of ml of PAO needed to titrate the sample.

N = the normality of the PAO used to titrate the sample.

V = the volume of sample taken (100 ml or a fraction thereof)

21,150 was calculated from the number of equivalents of iodine produced when the potassium iodide was added and from the rearrangement of the equation to produce the value in terms of mg/l.

8. Precision and Accuracy

- 8.1 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent, at concentrations of 1.6, 4.1, 6.6, 11.6 and 21.6 mg/l of iodide, the standard deviations were  $\pm 0.23$ ,  $\pm 0.17$ ,  $\pm 0.10$ ,  $\pm 0.06$  and  $\pm 0.50$  mg/l, respectively.
- 8.2 In a single laboratory (EMSL), using a mixed domestic and industrial waste effluent at concentrations of 4.1, 6.6, 11.6 and 21.6 mg/l of iodide, recoveries were 80, 97, 97 and 92%, respectively.

### Bibliography

1. Annual Book of ASTM Standards, Part 31", Water", Standard D1246-68, p 328, Method C (1976)
2. Bender, D. F., "Modification of the Iodimetric Titration Method for the Determination of Bromide and its Application to Mixed Domestic-Industrial Waste Effluent", Analyst (London) 100, p400-404 (June 1975).