Method 9.11 – Boiler water: chlorides (Cl^-) and sodium chloride (NaCl)

1. Rationale

The method is applicable to boiler water and determines the amount of chlorides in the sample as chlorides (Cl^-) and as sodium chloride (NaCl) in mg/litre.

2. Principle

The sample pH is adjusted to pH 9 with sulphuric acid using a phenolphthalein indicator. The solution is then titrated with silver nitrate ($AgNO_3$) in the presence of a chromate indicator. The silver ions will first react with all the chloride ions (to form AgCl) and then with the chromate ions at which point an orange colour will appear.

3. Apparatus

3.1 **Burette**: 10 cm^3

3.2 **Pipettes**: 10, 50 and 100 cm^3

3.3 **Conical flask**: 250 cm^3

3.4 **Volumetric flasks**: 2 × 100, 500 and 2 × 1 000 cm^3

3.5 **Analytical balance** readable to 0.0001 g

3.6 **Measuring cylinder**: 10 cm^3

4. Reagents

4.1 **Sulphuric acid solution** (0.1 M)

Sulphuric acid (H_2SO_4) is a corrosive acid. Contact with the skin, eyes and through inhalation must be avoided. Work in a fume cupboard while wearing gloves and safety glasses.

Measure 5.6 cm^3 hydrochloric acid in a measuring cylinder and transfer to a 1 000 cm^3 volumetric flask containing 500 cm^3 of distilled water. Acid must always be added to water and not the other way around. The dilution is exothermic and the solution will heat. Cool under running water and make to the mark with distilled water.

4.2 **Ethanol**

Ethanol (CH_3CH_2OH) is a flammable solvent, is toxic when swallowed and harmful to the eyes. Wear safety glasses during use.

4.3 Phenolphthalein indicator

Weigh 1.0 g phenolphthalein [$C_6H_4COOC(C_6H_4OH)_2$] powder in a 150 cm^3 beaker. Add 50 cm^3 of ethanol and dissolve. Transfer to a 100 cm^3 volumetric flask and make to the mark with ethanol.

4.4 Silver nitrate solution (0.0171 M)

Silver nitrate ($AgNO_3$) is corrosive. Wear gloves and safety glasses during use.

Dissolve 2.9049 g silver nitrate ($AgNO_3$) in distilled water. Transfer to a 1 000 cm^3 volumetric flask and make to the mark with distilled water. The silver nitrate solution is sensitive to light and should be stored in amber container.

4.5 Potassium chromate indicator solution (5%)

Potassium chromate (K_2CrO_4) is poisonous and corrosive to the eyes, skin and respiratory tract. Wear gloves and safety glasses during use.

Weigh 5.00 g of potassium chromate and dissolve in distilled water. Transfer to a 100 cm^3 volumetric flask and make to the mark.

5. Procedure

Pipette 50 cm^3 of the sample into a 250 cm^3 conical flask and add 2 drops of the phenolphthalein indicator solution. Add the 0.1 M sulphuric acid solution dropwise until the pink colour disappears.

Fill the burette with the 0.0171 M silver nitrate solution. Add 5 drops of the potassium chromate indicator to the solution in the conical flask. Titrate with the silver nitrate solution in the burette until the first orange tinge appears. Repeat the titration and record the average of the two titres.

6. Calculations

$$\text{Chlorides as NaCl (mg/litre)} = \frac{C_{AgNO_3} \times MM_{(NaCl)} \times 1000}{V_s} \times V_{titre}$$

$$= \frac{0.0171\ \text{M} \times 58.433\ \text{g/mole} \times 1000}{50\ \text{cm}^3} \times V_{titre}$$

$$= 20\ \text{mg/litre/cm}^3 \times V_{titre}$$

where C_{AgNO_3} ≡ Concentration of $AgNO_3$ (M or mole/litre)
$MM_{(NaCl)}$ ≡ Molecular mass of NaCl (g/mole)
V_s ≡ Volume of sample used (cm^3)
V_{titre} ≡ Volume of titre (cm^3)

$$\text{Chlorides as } Cl^- \text{ (mg/litre)} = \text{Chlorides as NaCl} \times \frac{MM_{(Cl^-)}}{MM_{(NaCl)}}$$

$$= \text{Chlorides as NaCl} \times \frac{35.443\ \text{g/mole}}{58.433\ \text{g/mole}}$$

= Chlorides as NaCl × 0.607

where $MM_{(NaCl)}$ ≡ Molecular mass of NaCl (g/mole)
$MM_{(NaCl)}$ ≡ Molecular mass of Cl (g/mole)

Report as mg/litre to the nearest unit.

7. Example

Volume of titre = 6.2 cm^3

Chlorides as NaCl = 20 mg/litre/cm^3 × 6.2 cm^3
= 124 mg/litre
Chlorides as Cl^- = 20 mg/litre/cm^3 × 6.2 cm^3 × 0.706
= 87.5 mg/litre

Report as 88 mg/litre Cl^-

8. References

Jeffery GH, Bassett J, Mendham J, and Denney RC (1989). *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed. Longman Scientific and Technical, Harlow, 343.

SASTA (1985). *Laboratory Manual for South African Sugar Factories*. 3rd Edition: 357.