Method 9.10 – Boiler water: alkalinity

1. Rationale

The method is applicable to boiler water. The alkalinity of a water sample is a measure of its capacity to neutralise acids and is the sum of all the titratable bases (hydroxides, carbonates and bicarbonates) at a specific pH. Alkalinity values provide guidance in applying proper dosages of chemicals in water and wastewater treatment processes such as coagulation and softening. Alkalinity is expressed as mg/litre $CaCO_3$.

2. Principle

The alkalinity of a boiler water sample is determined by titration with an acid solution using different indicators. Phenolphthalein or P-alkalinity is determined using phenolphthalein as an indicator which turns from a deep purple-red to colourless at around pH 9. Hydroxide or O-alkalinity is determined at the same pH but after precipitation of all the carbonates by the addition of barium chloride to measure the titratable hydroxides only. Total or M-alkalinity is determined using a total alkalinity indicator solution which turns from yellow to pink at pH 4.5. Hydroxide, carbonate or bicarbonate alkalinities may be calculated from the P- and M-alkalinities. Likewise, M-alkalinity may be calculated from the P- and O-alkalinities. It is, however, preferred to rather do three separate titrations.

3. Apparatus

3.1 **Burette**: 50 cm^3

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

3.3 **Conical flasks**: 3 × 250 cm^3

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

3.5 **Analytical balance** readable to 0.0001 g

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

4. Reagents

4.1 **Hydrochloric acid solution** (1 M)

Hydrochloric acid (HCl) 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 8.9 cm^3 hydrochloric acid in a measuring cylinder and transfer to a 100 cm^3 volumetric flask containing 40 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 Hydrochloric acid solution (0.02 M)

Pipette 10 cm^3 of the 1 M hydrocholric acid solution into a 500 cm^3 volumetric flask and make to the mark with distilled water.

4.3 Ethanol

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

4.4 Phenolphthalein indicator

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

4.5 Barium chloride powder

Barium chloride ($BaCl_2 \cdot 2H_2O$) is an irritant and harmful when swallowed, absorbed through the skin and when in contact with the eyes. Wear gloves and safety glasses during use.

4.6 Total alkalinity indicator

Dissolve 0.0200 g methyl red [$(CH_3)_2NC_6H_4N_2C_6H_4COOH$] and 0.1000 g of the sodium salt of bromochresol green [$Br_2OHC_6H_2C(C_6H_4SO_3H)C_6H_2OBr_2$] in 100 cm^3 distilled water.

5. Procedure

5.1 P-alkalinity

Fill the burette with the 0.02 M hydrochloric acid solution. Pipette 50 cm^3 of the sample into a 250 cm^3 conical flask and add 2 drops of the phenolphthalein indicator solution. Titrate with the 0.02 M hydrochloric acid solution in the burette. Repeat the titration and record the average of the two titres.

5.2 O-alkalinity

Fill the burette with the 0.02 M hydrochloric acid solution. Pipette 100 cm^3 of the sample into a 250 cm^3 conical flask and add sufficient barium chloride to precipitate the carbonates (until no more solids are formed). Add 2 drops of the phenolphthalein indicator solution and titrate with the 0.02 M hydrochloric acid solution in the burette. Repeat the titration and record the average of the two titres.

5.3 M-alkalinity

Fill the burette with the 0.02 M hydrochloric acid solution. Pipette 100 cm^3 of the sample into a 250 cm^3 conical flask and add 2 drops of the total alkalinity indicator solution. Titrate with the 0.02 M hydrochloric acid solution in the burette. Repeat the titration and record the average of the two titres.

6. Calculations

6.1 P-alkalinity

$$\text{P-alkalinity} = \frac{C_{HCl}}{2} \times \frac{MM_{(CaCO_3)} \times 1000}{V_s} \times V_{titre}$$

$$= \frac{0.02\ \text{M}}{2} \times \frac{100\ \text{g/mole} \times 1000}{50\ \text{cm}^3} \times V_{titre}$$

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

where C_{HCl} ≡ Concentration of HCl (M or mole/litre)
$MM_{(CaCO_3)}$ ≡ Molecular mass of $CaCO_3$ (g/mole)
V_s ≡ Volume of sample used (cm^3)
V_{titre} ≡ Volume of titre (cm^3)

6.2 O-alkalinity

$$\text{O-alkalinity} = \frac{C_{HCl}}{2} \times \frac{MM_{(CaCO_3)} \times 1000}{V_s} \times V_{titre}$$

$$= \frac{0.02\ \text{M}}{2} \times \frac{100\ \text{g/mole} \times 1000}{100\ \text{cm}^3} \times V_{titre}$$

$$= 10\ \text{mg/litre/cm}^3 \times V_{titre}$$

where C_{HCl} ≡ Concentration of HCl (M or mole/litre)
$MM_{(CaCO_3)}$ ≡ Molecular mass of $CaCO_3$ (g/mole)
V_s ≡ Volume of sample used (cm^3)
V_{titre} ≡ Volume of titre (cm^3)

6.3 M-alkalinity

$$\text{M-alkalinity} = \frac{C_{HCl}}{2} \times \frac{MM_{(CaCO_3)} \times 1000}{V_s} \times V_{titre}$$

$$= \frac{0.02\ \text{M}}{2} \times \frac{100\ \text{g/mole} \times 1000}{100\ \text{cm}^3} \times V_{titre}$$

$$= 10\ \text{mg/litre/cm}^3 \times V_{titre}$$

where C_{HCl} ≡ Concentration of HCl (M or mole/litre)
$MM_{(CaCO_3)}$ ≡ Molecular mass of $CaCO_3$ (g/mole)
V_s ≡ Volume of sample used (cm^3)
V_{titre} ≡ Volume of titre (cm^3)

7. Example

M-alkalinity

Volume of titre = 15.2 cm^3

M-alkalinity = 10 mg/litre/cm^3 × 15.2 cm^3
= 152 mg/litre

Report as 152 mg/litre $CaCO_3$

8. References

Anon (2005). *Alkalinity* at: http://www.primeindia.com/manav/mangt9.html, April.

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SASTA (1985). *Laboratory Manual for South African Sugar Factories*. 3rd Edition: 354 - 355.