Method 11.2 – Miscellaneous: total and basic lead in lead sub-acetate

1. Rationale

The method is applicable to dry lead sub-acetate powder and lead sub-acetate solutions and determines the total and basic lead content of the sample in two separate titrations. According to specification the total lead content of the lead acetate must be 24.4 ± 1.0 g PbO/100 cm^3 and the basic lead content must be between 9.5 and 10.5 g PbO/100 cm^3. Lead sub-acetate is also called basic lead acetate.

2. Principle

The total lead is determined through a complexation titration of the lead ions with EDTA in the presence of a HMTA buffer solution to ensure a pH of between 5.0 and 6.0. The resulting lead concentration is expressed as lead oxide according to convention by applying a conversion factor. The basic lead is determined by addition of a stoichiometric volume of EDTA solution as determined in the total lead titration. The liberated acetate ions are titrated with sodium hydroxide to determine the basic lead content of the sample. The resulting lead concentration is expressed as lead oxide according to convention by applying a conversion factor.

3. Apparatus

3.1 **Analytical balance** readable to 0.0001 g

3.2 **Drying oven** operating at 105°C

3.3 **Desiccator** with self-indicating silica gel

3.4 **Pestle and mortar**

3.5 **Pipettes**: 10 and 20 cm^3

3.6 **Volumetric flasks**: 100, 200 and 1 000 cm^3

3.7 **Burettes**: 4 × 50 cm^3

3.8 **Conical flasks**: 4 × 250 cm^3

3.9 **Spatula**: non-metal

3.10 **Beaker**: 100 cm^3

3.11 **Funnel**: 100 mm ϕ

3.12 **pH meter**

3.13 **Filter paper**: Whatman No. 6, Postslip medium white or equivalent, 185 mm ϕ

4. Reagents

4.1 Water: carbon dioxide free distilled or deionised

4.2 pH buffer solutions: 4 and 7

4.3 Lead nitrate solution (0.05 M)

Lead nitrate [$Pb(NO_3)_2$] is poisonous and harmful to human health and the environment. Do not inhale, swallow or bring in contact with the skin or eyes. Wear safety glasses, gloves and a dust mask during handling.

Dry lead nitrate for 2 hours at 105°C. Cool in a desiccator for 1 hour and weigh 3.3123 g accurately in a beaker. Transfer quantitatively with deionised water to a 200 cm^3 volumetric flask. Make to the mark and mix.

4.4 Ethylene diamine tetra acetic acid, disodium salt dihydrate (0.05 M)

Ethylene diamine tetra acetic acid (EDTA), disodium salt dihydrate is mildly irritating to the skin, eyes and respiratory tract.

Weigh 18.612 g EDTA, dissolve in distilled water and dilute to 1 000 cm^3 in a volumetric flask.

4.5 Hexamethylenetetramine buffer solution (1.0 M)

Hexamethylenetetramine [HMTA, $(CH_2)_6N_4$] is harmful to human health and is corrosive to the skin, eyes and respiratory tract. Use gloves and safety glasses during handling.

Dissolve 140.0 g HMTA in deionised water and dilute to 1 000 cm^3 in a volumetric flask. The HMTA solution is used to keep the pH of the solution between 5.0 and 6.0.

4.6 Sodium hydroxide solution (1.0 M)

Sodium hydroxide (NaOH) is a corrosive base and contact with the skin and eyes must be avoided. Use gloves and safety glasses during handling.

Weigh 40 g sodium hydroxide pellets accurately to 0.0001 g and dissolve in some distilled water. This dissolution is exothermic and the solution will therefore heat. Allow the solution to cool and dilute to 1 000 cm^3 in a volumetric flask.

4.7 Sodium hydroxide solution (0.1 M)

Sodium hydroxide (NaOH) is a corrosive base and contact with the skin and eyes must be avoided. Use gloves and safety glasses during handling.

Weigh 4.0 g sodium hydroxide pellets accurately to 0.0001 g and dissolve in some distilled water. This dissolution is exothermic and the solution will therefore heat. Allow the solution to cool and dilute to 1 000 cm^3 in a volumetric flask.

4.8 Potassium nitrate (KNO_3)

4.9 Metal indicator (solid)

Grind 0.10 g xylenol orange and 9.90 g potassium nitrate together and keep in a tightly stoppered bottle.

4.10 Methylene blue indicator (1%)

Weigh 1.0 g methylene blue $\{[(CH_3)_2NC_6H_3NSC_6H_3N(CH_3)_2]^+Cl^-\}$ and dissolve in distilled water. Transfer to a 100 cm^3 volumetric flask and make to the mark.

4.11 Mixed indicator solution (pH 7.4)

Solution A: dissolve 0.1 g of the sodium salt of bromothymol blue ($C_{27}H_{28}Br_2O_5S$) in 100 cm^3 distilled water.

Solution B: Dissolve 0.1 g of the sodium salt of phenol red ($C_{19}H_{14}O_5S$) in 100 cm^3 distilled water.

Mix equal volumes of solutions A and B.

4.12 Acetic acid (1.0 M)

Acetic acid (CH_3COOH) is a corrosive acid and contact with the skin and eyes must be avoided. Wear safety glasses and gloves during handling.

Measure 57 cm^3 glacial (concentrated) acetic acid accurately in a measuring cylinder and add to a 1 000 cm^3 volumetric flask containing 500 cm^3 of distilled water. Make to the mark with distilled water.

5. Procedure

5.1 Standardisation of the 0.05 M EDTA solution

Fill the burette with the EDTA solution. Pipette 20 cm^3 of the lead nitrate solution into a 250 cm^3 conical flask. Using a measuring cylinder add 20 cm^3 of the HMTA solution as a buffer. Add 0.1 g of the solid metal indicator and 4 drops of methylene blue indicator. Titrate with the EDTA solution. The endpoint coincides with the first appearance of a green colour. Repeat the titration. The repeat titres should agree to within 0.1 cm^3. Record the average titre, V_{EDTA}.

5.2 Calibration of the pH meter

Do a two-point calibration of the pH meter at pH 4 and 7 using fresh buffer solutions on a daily basis.

5.3 Sample preparation

Lead salts are poisonous and harmful to human health and the environment. Do not inhale, swallow or bring in contact with the skin or eyes. Wear safety glasses, gloves and a dust mask during handling.

5.3.1 Dry lead sub-acetate

Fill a 50 cm^3 burette with the acetic acid solution. Weigh 3 g of the lead sub-acetate powder accurately to 0.001 g in a beaker. Add sufficient acetic acid from the burette with the aid of the pH meter to bring the pH to between 5.0 and 6.0. Note the volume of acetic acid added.

Refill the burette with acetic acid and add an equivalent volume of the acetic acid used above to a 200 cm^3 volumetric flask. Pipette 10 cm^3 of the filtered lead solution and 100 cm^3 distilled water to the volumetric flask. If the solution is not clear, add more acetic acid until a clear solution is obtained. Note the total volume of acetic acid used, V_{AcOH}. Make to the mark with distilled water and mix.

5.3.2 Lead sub-acetate solution

Fill a 50 cm^3 burette with the acetic acid solution. Decant about 50 cm^3 of the lead solution and filter through filter paper supported in a funnel. Discard the first 10 cm^3 and collect the rest of the filtrate in a clean, dry beaker. Pipette 10 cm^3 of the filtrate into a 100 cm^3 beaker and add sufficient acetic acid from the burette with the aid of the pH meter to bring the pH to between 5.0 and 6.0. Note the volume of acetic acid added.

Refill the burette with acetic acid and add an equivalent volume of the acetic acid used to a 200 cm^3 volumetric flask. Pipette 10 cm^3 of the filtered lead solution and 100 cm^3 distilled water to the volumetric flask. If the solution is not clear, add more acetic acid until a clear solution is obtained. Note the total volume of acetic acid used, V_{AcOH}. Make to the mark with distilled water and mix.

5.4 Determination of the total lead content

Pipette 20 cm^3 of the sample solution into a 250 cm^3 conical flask. Add 20 cm^3 of the HMTA buffer solution using a measuring cylinder, 0.1 g of the metal indicator and 4 drops of methylene blue indicator.

Titrate the mixture against the EDTA solution in the burette. A white precipitate will appear but will dissolve before the endpoint is reached. The purple colour of the mixture will suddenly change to a neutral grey and then to green. The endpoint coincides with the first appearance of the green colour. Repeat the titration. The repeat titres should agree to within 0.1 cm^3. Record the average titre, V_{EDTA}.

5.5 Determination of the basic lead content

Fill one 50 cm^3 burette with the EDTA solution and a second with the 0.1 M sodium hydroxide solution. Pipette 20 cm^3 of the sample solution into a 250 cm^3 conical flask. Add an equivalent volume to the titre obtained during the determination of the total lead content (V_{EDTA}) of the EDTA solution from the first burette to the conical flask.

Add 3-4 drops of the mixed indicator solution and titrate with the sodium hydroxide solution in the second burette. The solution colour will change from yellow through neutral grey to purple. The endpoint coincides with the first appearance of the purple colour. Repeat the titration. The repeat titres should agree to within 0.1 cm^3. Record the average titre, V_{NaOH}.

6. Calculations

6.1 EDTA standardisation

$$\text{EDTA concentration (M)} = \frac{V_{aliquot}}{V_t} \times C_{Pb}$$

where $V_{aliquot}$ ≡ Volume of the lead nitrate solution (cm^3)
V_t ≡ Volume of the titre (cm^3)
C_{Pb} ≡ Concentration of the lead nitrate solution (M)

The molecular weight of lead (Pb) is 207.19 g/mole. Therefore, 1 cm^3 of the 0.05 M lead solution contains 10.3595 mg lead.

A 1 cm^3 volume of the 0.05 M lead solution will complex with 1 cm^3 of the EDTA solution. Therefore, 1 cm^3 of a 0.05 M EDTA solution will complex 10.3595 mg lead.

$$\text{Equivalent mass of lead (mg)} = 10.3595\ \text{mg} \times \frac{\text{actual EDTA (M)}}{0.05\ \text{M EDTA}}$$

6.2 Total lead

$$\text{Lead Pb (\%)} = \text{titre} \times \frac{200\ \text{cm}^3}{\text{mass (g)} \times 20\ \text{cm}^3} \times \frac{\text{equivalent lead (mg)}}{1000} \times 100$$

$$= \frac{\text{titre} \times \text{equivalent lead (mg)}}{\text{mass (g)}}$$

$$\text{Lead PbO (\%)} = \text{Lead Pb (\%)} \times \frac{MM_{(PbO)}}{MM_{(Pb)}}$$

$$= \text{Lead Pb (\%)} \times \frac{223.2\ \text{g/mole}}{207.2\ \text{g/mole}}$$

$$= \text{Lead Pb (\%)} \times 1.077$$

where $MM_{(PbO)}$ ≡ Molecular mass of PbO (g/mole)
$MM_{(Pb)}$ ≡ Molecular mass of Pb (g/mole)

6.3 Basic lead

$$\text{Basic Pb (\%)} = [V_{EDTA} - (V_{NaOH} - V_{AcOH})] \times \frac{200\ \text{cm}^3}{\text{mass (g)} \times 20\ \text{cm}^3} \times \frac{\text{eq lead (mg)}}{1000} \times 100$$

$$= \frac{[V_{EDTA} - (V_{NaOH} - V_{AcOH})] \times \text{equivalent lead (mg)}}{\text{mass (g)}}$$

where V_{EDTA} ≡ Titre volume of EDTA determined in 5.4 (cm^3)
V_{NaOH} ≡ Titre volume of NaOH determined in 5.5 (cm^3)
V_{AcOH} ≡ Volume of AcOH used in 5.3.1 or 5.3.2 (cm^3)

$$\text{Basic PbO (\%)} = \text{Basic Pb (\%)} \times \frac{MM_{(PbO)}}{MM_{(Pb)}}$$

$$= \text{Basic Pb (\%)} \times \frac{223.2\ \text{g/mole}}{207.2\ \text{g/mole}}$$

$$= \text{Basic Pb (\%)} \times 1.077$$

where $MM_{(PbO)}$ ≡ Molecular mass of PbO (g/mole)
$MM_{(Pb)}$ ≡ Molecular mass of Pb (g/mole)

7. Example

7.1 EDTA standardisation

Titre of EDTA standardisation = 19.6 cm^3

$$\text{EDTA concentration (M)} = \frac{20.00\ \text{cm}^3}{19.60\ \text{cm}^3} \times 0.05\ \text{M}$$

$$= 0.05102\ \text{M}$$

$$\text{Equivalent mass of Pb (mg)} = 10.3595\ \text{mg} \times \frac{0.05102\ \text{M}}{0.05\ \text{M}}$$

$$= 10.5708\ \text{mg}$$

7.2 Total lead

Mass of lead = 3.0036 g
EDTA titre = 21.3 cm^3

$$\text{Total Pb} = \frac{21.3\ \text{cm}^3 \times 10.5708\ \text{mg}}{3.0036\ \text{g}}$$

$$= 74.96\%$$

Total PbO = 80.73%

Report as 81%

7.3 Basic lead

Mass of lead = 3.0036 g
EDTA titre (V_{EDTA}) = 21.3 cm^3
NaOH titre (V_{NaOH}) = 24.5 cm^3
AcOH titre (V_{AcOH}) = 12.6 cm^3

Basic Pb = 33.08%

Basic PbO = 35.63%

Report as 36%

8. References

ICUMSA (1994). Determination of lead in basic lead acetate solution. Appendix 2 in: The determination of the polarisation of raw sugar by polarimetry. *Method GS1/2/3-1*.

SASTA (1985). *Laboratory Manual for South African Sugar Factories*. 3rd Edition: 170, 173 - 174, 176, 206 - 209.