

DRAFT TANZANIA STANDARD

TBS/CDC 7 (1280) P3 Methods of test for chemical analysis of Limestone and Limestone products.

TANZANIA BUREAU OF STANDARDS

DRAFT FOR STAKEHOLDERS COMMENTS ONLY

FOREWORD

This Draft Tanzania Standard is being developed by the Industrial and Laboratory Chemicals Technical Committee under supervision of the Chemicals Standards Divisional Committee and it is in accordance with the procedures of the Bureau.

This draft Tanzania Standard has been prepared with assistance drawn from:

KS 03 – 221: 1983 Specification for lime for chemical industry; published by Kenya Bureau of Standards

MS 850:1997 Methods of test for limestone, quicklime and hydrated lime polyaluminium-based coagulants, published by Department of Standards of Malaysia and

BS 6463-102:2001 Quicklime, hydrated lime and natural calcium carbonate. Methods for chemical analysis published by British Standards Institution.

IS 1514: 2010 Method of Sampling and test for quicklime and hydrated lime published by Indian Bureau of Standards

In reporting the test results of a test or analysis made in accordance with this standard, if final value, calculated or observed is to be rounded off, it shall be done in accordance with TZS 4 *Rounding off numerical values*.

Methods of test for chemical analysis of limestone and limestone products.**1. Scope**

This draft Tanzania Standard covers chemical analysis of limestone and limestone products.

2. Normative references

The following referenced documents are indispensable for the application of this document; the latest edition of the referenced document (including any amendments) applies;

TBS/CDC-7 (3736) P3 *Standard terminology relating to Lime and Limestone (as used by the industry)*

TZS 59/ISO 3696 *Water for analytical laboratory use – Specification and test method Water distilled quality – Specification.*

TBS/CDC 7(5418) P3 *Methods of sampling lime and limestone products.*

3. Terminologies

For the purpose of this standard, terminologies from TBS/CDC-7 (3736) P3 shall apply

4. Sampling

Samples for chemical analysis shall be taken and prepared in accordance with the requirements of TBS/CDC 7(5418) P3 (see clause 2).

5. Quality of reagents

Unless specified otherwise, analytical grade chemicals and distilled water (conforming to TZS 59/ISO 3696) shall be employed.

6. Determination of loss on ignition**6.1 Procedure**

(a) Weigh to the nearest milligram, 1g of the rough ground test sample. ignite it to constant mass at a temperature between 900 °C and 1000 °C in a tarred platinum crucible of 20 mL to 30 mL capacity covered with a well-fitting lid. Allow 10 min for the initial ignition period and 5 min for subsequent period.

(b) After each ignition, cool it on a copper block in an efficient desiccator and weigh it as rapidly as possible to the nearest milligram, (three decimal places).

6.2 Calculation

Loss on ignition,

$$\text{percent by mass} = 100 \frac{(M_1 - M_2)}{M_1}$$

where,

M_1 represents the mass, in g, of the material taken for the test
 M_2 represents the mass, in g, of the material after Ignition

NOTE: Quicklime and hydrated lime are highly reactive and all effort shall be made to prevent absorption of carbon dioxide and moisture by the sample.

7. Determination of available lime (as CaO) in quicklime

7.1 General

Two methods have been prescribed for the determination of available lime. For routine analysis, the iodine method may be used but in case of dispute, the sugar method shall be used.

7.2 Iodine method

7.2.1 Reagents

- (a) Standard sodium thiosulphate solution – 0.1 M, freshly standardized.
- (b) Standard iodine solution – 1 M, freshly standardized against standard sodium thiosulphate solution.
- (c) Starch indicator solution – Triturate 5 g of starch and 0.01 g of mercuric iodide with 30 mL of cold water and slowly pour it while stirring into 1 litre of boiling water. Boil for 3 min then allow the solution to cool and decant off the supernatant clear liquid.
- (d) Distilled water free from carbon dioxide.

7.2.2 Procedure

Take 1 g of the material, accurately weighed, in a glass-stoppered conical flask and add about 30 mL of boiling water. Shake for 5 to 10 min. Cool the solution and add an amount of iodine solution sufficient to provide an excess of about 5 mL and stir occasionally until the lime has gone in solution. Any insoluble silica present is easily distinguished from the milky-appearing lime. When the solution of lime is complete (about 10 minutes are required), dilute the solution in a volumetric flask to 500 mL. Pipette out 25 mL of the solution and titrate the excess iodine with standard sodium thiosulphate solution, adding starch indicator towards the end of the titration. Carry out a blank determination using the same amount of iodine solution as with the sample

7.2.3 Calculation

Available lime (as CaO), percent by mass

$$= \frac{56.08 (V_1 - V_2) M}{m}$$

where,

V_1 represents volume in mL of standard sodium thiosulphate solution used in the blank;

V_2 represents volume in mL of standard sodium thiosulphate solution used with the material;

M represents molarity of standard sodium thiosulphate solution; and

m represents the mass in g of the material taken for the test.

7.3 Sugar method

7.3.1 Apparatus

Flask shaker.

7.3.2 Reagents

- (a) Rectified spirit
- (b) Standard hydrochloric acid – 0.1 M.
- (c) Standard sodium hydroxide solution – 0.1 M.
- (d) Sugar solution –15 % m/v in carbon dioxide-free water.
- (e) Phenolphthalein in 100 mL of rectified spirit.

7.3.3 Procedure

Weigh accurately about 1 g of finely powdered material into a 500 mL volumetric flask and wet it with the minimum amount of rectified spirit. Shake with about 400 mL of sugar solution for 3 hours continuously with a flask shaker. Make up volume to the mark. Filter through a coarse dry filter paper (Whatman No. 40 or equivalent) into a dry flask. Discard the first 25 mL of the filtrate. Pipette out 50 mL from the filtrate into another flask to which 50 mL standard hydrochloric acid is added and titrate with standard sodium hydroxide solution using phenolphthalein as indicator.

Run a blank using 50 mL of sugar solution and 50 mL of standard hydrochloric acid.

7.3.4 Calculation

Available lime (as CaO) percent by mass

$$= \frac{28.04 (A - B) M}{m}$$

where,

A represents the volume in mL of standard sodium hydroxide solution used in the blank solution;

B represents volume of standard sodium hydroxide solution used with the material;

M represents the molarity of standard sodium hydroxide solution; and

m represents mass in g of the material taken for the test.

8. Determination of available lime in hydrated lime

8.1 General

Two methods for the determination of available lime in hydrated lime are prescribed, namely:

- (a) iodine method for routine analysis, and
- (b) sugar method for cases of dispute.

8.2 Iodine method (see 7.2)

8.3 Sugar method (see 7.3)

9. Determination of volatile matter in hydrated lime at 105 °C

9.1 Apparatus

- (a) Platinum or silica dish – 30 mL;
 (b) Electric drying oven – Capable of maintaining a temperature of 105 °C.

9.2 Procedure

Weigh accurately, to the nearest 0.01 g, about 1 g of the finely powdered sample in a platinum or silica dish. Place it in an oven maintained at 105°C ± 2 °C and dry to constant mass.

9.3 Calculation

Volatile matter at 105 °C percent by mass

$$= \frac{(m_1 - m_2) 100}{m_1}$$

where,

m_1 represents mass in g of the material taken for the test; and

m_2 represents mass in g of the sample after drying.

10. Determination of silica and acid insoluble

10.1 Determination of acid insoluble

10.1.1 Reagent

Concentrated hydrochloric acid.

10.1.2 Procedure

Transfer 1.000 g of lime to a beaker and pour over it to 50 mL of water, mix well and add 10 mL to 15 mL of concentrated hydrochloric acid. Boil for 15 min, filter and wash thoroughly with hot distilled water until the washings are free from chlorides. Transfer the residue carefully into a previously weighed platinum crucible. Place the dish containing the residue in an electric furnace and allow the temperature to rise slowly until 1000 °C ± 50 °C is reached. Keep at this temperature for about 15min, remove the dish from the furnace, cool in a desiccator and weigh. Repeat heating to constant mass.

10.1.3 Calculation

Silica and acid insoluble, percent by mass

$$= \frac{m_1 \times 100}{m_2}$$

where,

m_1 represents mass in g of the residue after calcination, and

m_2 represents mass in g of the sample for the test.

10.2 Determination of silica

10.2.1 Procedure

In a suitable dish containing 50 mL of distilled water add 1.000 g of lime, mix well and add 10 mL to 15 mL of concentrated hydrochloric acid. Evaporate the solution to dryness for about one hour at 200 °C in case of a high calcium lime, or at 120 °C for a high magnesium lime. Cool, moisten thoroughly with concentrated hydrochloric acid and let it stand for a few minutes, add an equal volume of water, cover the dish and heat on the steam bath for 10 min to 15 min.

Filter out the silica, wash well with dilute hydrochloric acid and then wash thoroughly with hot water until the washings are free from chlorides.

Evaporate the filtrate to dryness, take up with hydrochloric acid as before and filter through a small paper and wash as stated above. Keep the filtrate for test under clause 11.3.

Transfer both filter papers containing the silica residue into a previously weighed platinum crucible. Place the crucible on a hot plate until the contents are dried and carefully char the papers.

Ignite in a furnace at $1000\text{ }^{\circ}\text{C} \pm 50\text{ }^{\circ}\text{C}$ starting with low heat to burn off papers. Cool in a desiccator and weigh to constant mass.

Add about 2 mL of water, 2 to 3 drops of approximately 5 M sulfuric acid and 5 mL of 40 % hydrofluoric acid. Evaporate to dryness and ignite to constant mass. If necessary, repeat the treatment with smaller quantity of hydrofluoric acid to ensure constancy in mass.

10.2.2 Calculation

$$\text{Silica percent by mass} = \frac{m}{M} 100$$

Where,

m represents loss in mass of the residue on treatment by hydrofluoric acid

M represents mass of the sample

11. Determination of iron oxide and alumina

11.1 Apparatus

- (a) Platinum crucible
- (b) Desiccator
- (c) Bunsen burner

11.2 Reagents

- (a) Concentrated hydrochloric acid.
- (b) Ammonium hydroxide – Approximately 4M.
- (c) Standard potassium permanganate – 0.02 M.

11.3 Procedure

To the filtrate preserved under clause 10.2.1, add concentrated hydrochloric acid, if necessary, in sufficient amount to make the total amount equivalent to 10 mL-15 mL of concentrated hydrochloric acid. Dilute to 200 mL-250 mL and heat to boiling, add a very slight excess ammonium hydroxide and keep just below the boiling point until the odour of ammonia is barely perceptible. Filter off the iron and aluminium hydroxide while hot, collecting the filtrate in a 250-mL volumetric flask. Wash with hot water, ignite the residue in a platinum crucible, cool in a desiccator and weigh as aluminium oxide and ferric oxide. Make up the filtrate to 250 mL and preserve the filtrate for test under clause 12.2.2.2.

11.3.1 Iron oxide

11.3.1.1 Fuse the combined aluminium and ferric oxide in a platinum crucible with 3 g to 4 g of potassium bisulphate using a Bunsen burner. Dissolve in water, add sufficient sulfuric acid to make a 5 % solution and through the Jones reductor. Cool and titrate with standard potassium permanganate solution.

11.3.1.2 Calculation

$$\text{Iron oxide (as Fe}_2\text{O}_3\text{), percent by mass} = \frac{78.85 VM}{m}$$

where,

V represents volume in mL of standard potassium permanganate solution used;
M represents the molarity of standard potassium permanganate solution; and
m represents mass in g of the material taken for the test (see clause 10.2.1).

11.3.2 Aluminium oxide – Subtract the ferric oxide value from the combined oxide value (see clause 11.3.1.2).

12. Determination of burnt lime (as CaO)

12.1 Procedure

Determine the available lime, sulphates and carbon dioxide as prescribed in clauses 7 or 8, 12.4 and 17 respectively and total calcium oxide as given in clause 12.2.

12.2 Determination of total Calcium Oxide

12.2.1 Methods

Two methods have been prescribed:

- (a) Method A is the classical method, and
- (b) Method B is the complexometric method.
- (c) However, in case of dispute, method A shall be followed.

12.2.2 Method A

12.2.2.1 Reagents

- (a) Ammonium oxalate solution – Saturated.
- (b) Dilute aqueous ammonia solutions – Approximately 5 M and 1 M.
- (c) Dilute hydrochloric acid – Approximately 5 M.
- (d) Dilute sulfuric acid - Approximately 3 M.
- (e) Dilute potassium permanganate solution - Approximately 0.002 M.
- (f) Standard potassium permanganate solution – 0.02 M.
- (g) Diammonium hydrogen phosphate – Approximately 25 % (m/v).
- (h) Concentrated aqueous ammonia solution.

12.2.2.2 Procedure

Pipette out 50 mL of the filtrate preserved under clause 11.3 in a beaker and dilute to 100 mL. Heat to boiling and add slowly about 35 mL of boiling ammonium oxalate solution. Continue boiling for 2 or 3 min and allow the precipitated calcium oxalate to settle for half an hour. Filter the precipitated calcium oxalate through Whatman No. 42 filter paper or its equivalent.

Wash thoroughly with small portions of 1 M aqueous ammonia solution and then with hot water until the washings do not decolourise a hot dilute potassium permanganate solution in the presence of dilute sulfuric acid.

Preserve the filtrate and washings for test in clause 13.2.2. Puncture the filter paper and transfer the precipitate to the beaker already used for precipitation with a fine jet of hot water. Add about 50 mL of dilute sulfuric acid, heat to 60 °C and titrate with standard potassium permanganate solution with constant stirring. Towards the end of the titration, introduce the filter paper, which was used for filtration into the titration vessel, and carry out the blank with all reagents following the procedure as outlined for this method.

12.2.2.3

In case of magnesium limes, decant through a filter paper, redissolve the calcium oxalate in the beaker in the filter paper with dilute hydrochloric acid and the filter paper four times with hot water and finally with 1 M aqueous ammonia solution, dilute the acid solution to 250 mL, bring to boil, add a few millilitres of 5 M aqueous ammonia solution in slight excess and proceed as in clause

12.2.2.2

For the second filtration, use the same filter paper as was used before.

12.2.2.4

If it is desired to complete the analysis in as short a time as possible, a portion of 50 mL of the filtrate from ferric oxide and aluminium oxide, determination should be precipitated in the usual way with excess of ammonium oxalate. Boil for 5 min and let the calcium oxalate settle clear. Decant through a qualitative filter paper (Whatman No. 42) and cool the filtrate (with ice water if possible). Add diammonium hydrogen phosphate solution in large excess and 5 to 10 mL of concentrated ammonia solution, stir rapidly with rubber 'policeman'.

From the amount of precipitate thus formed one may judge whether the lime contains sufficient magnesium oxide to require a double precipitation or not. For accurate work, if there is more than a slight amount of magnesium oxide, a double precipitation shall be carried out using fresh 50 mL aliquot.

12.2.2.5 Calculation

Total calcium oxide (as CaO), percent by mass

$$= \frac{14.02(V_2 - V_1)N}{m}$$

where,

V_1 represents the volume in mL of standard potassium permanganate solution used for the test;

V_2 represents volume in mL of standard potassium permanganate solution used for the blank;

N represents the normality of standard potassium permanganate solution; and

m represents mass in g of the material taken for the test (see clause 10.2.1).

12.2.3 Method B

12.2.3.1 Reagents

- (a) Concentrated hydrochloric acid;

- (b) Standard disodium ethylene diamine tetra-acetate (EDTA) solution – Weigh 7.44 g disodium ethylene diamine tetra-acetate dihydrate and dissolve in water. Make up the volume to 2 litres. Standardize the solution against standard calcium chloride solution according to the procedure given in clause 12.2.3.2.
- (c) Standard calcium chloride solution – Dry about 2 g of calcium carbonate at 120 °C to constant mass and dissolve 1.000 g of the dried calcium carbonate in a 10 mL of concentrated hydrochloric acid, (1:1) and then make up the volume to 1 litre. One millilitre of this solution is equivalent to 0.00056 g of calcium oxide.
- (d) Eriochrome black T indicator – Dissolve 0.1 g of the dye in 20 mL of methanol. This solution shall be prepared freshly every week. Store in a cool place.
- (e) Murexide indicator – Grind 0.2 g of murexide with 10g of sodium chloride until the mixture is homogenous.

OR

- Calcein indicator – Grind 0.01 g of calcein thoroughly with 1 g of potassium chloride.
- (f) Buffer solution – Dissolve 67.5 g of ammonium chloride in a mixture of 520 mL of water. Dissolve a mixture of 0.931 g of disodium ethylene diamine tetra-acetate dihydrate and 0.616 g of magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in 50 mL of water, combine both the solutions and make up to 1 litre. Five millilitres of buffer solution, added to 50 mL of distilled water, should not consume more than a drop of EDTA solution to change to distinct blue with eriochrome black T indicator.
 - (g) Standard sodium hydroxide solution 5 M.

12.2.3.2 Standardization of disodium ethylene diamine tetra-acetate (EDTA) solution

Standardize as follows:

- (a) With murexide or calcein indicator, pipette out 50 mL of standard calcium chloride solution (see Note 1) in a 250mL conical flask and add to it 1.0 mL of standard sodium hydroxide solution to adjust the pH of the solution to about 12. Add 0.1 g to 0.2 g of murexide indicator (see Note 2) and titrate the solution against EDTA solution until the colour changes from pink to purple.
- (b) With eriochrome black T indicator, pipette out 50 mL of standard calcium chloride solution (see Note 1) in a 250mL conical flask and add 5 mL of buffer solution to adjust the pH of the solution to approximately 10. Add 5 drops of eriochrome black T indicator and titrate against standard EDTA solution until the wine-red colour changes to pure blue. (The volume of the solution to be titrated against the EDTA solution should be approximately 50 mL and the strength of the standard ETDA should be adjusted in such a way that most 50 mL of it is required for titration).

NOTES: 1. The aliquot for titration shall have a pH 7 so that by adding standard sodium hydroxide or buffer solution the desired pH could be adjusted in the solution.

2. If calcein indicator is to be used in place of murexide indicator, add 0.07 g of calcein. The colour change in this case will be from greenish yellow fluorescence to brown.

12.2.3.3 Prepared sample solution

Dissolve about 2.5 g of the material, accurately weighed, in a limited quantity of concentrated hydrochloric acid and make up the volume to one litre. Reserve the prepared sample solution for the determination of magnesium oxide in Clause 13.2.

12.2.3.4 Procedure

Pipette out 100 mL of the prepared sample solution (see Clause 12.2.3.3) in a conical flask and dilute with 40 mL of water. Add 1.5 mL of standard sodium hydroxide solution followed by a small quantity (0.1 to 0.2 g) of murexide indicator (0.07 g of calcein indicator). Titrate against standard EDTA solution till the colour changes from wine red to purple. (In the case of calcein indicator the colour changes will be from greenish yellow fluorescence to brown.) Note the burette reading.

12.2.3.5 Calculation

Total calcium oxide (as CaO), percent by mass

$$= \frac{10\,000 V_1 A_1}{m}$$

where,

V_1 represents the volume in mL of standard EDTA solution used;
 A_1 represents the mass in g of calcium oxide equivalent to 1 mL of standard EDTA solution as obtained in Clause 12.2.3.2; and
 m represents mass in g of the material taken as in Clause 12.2.3.3.

12.3 Calculation of results

12.3.1 Convert the percentage of carbon dioxide present to its equivalent percentage of CaO by multiplying with the factor 1.275.

12.3.2 Convert the percentage of sulphates present as determined by Clause 12.4 to its equivalent percentage of CaO by multiplying with the factor 0.5837.

12.3.3 To obtain dead burnt lime (as CaO), subtract total available lime (as CaO) and the values obtained in Clause 12.3.1 and 12.3.2 from the percentage of total calcium oxide (as CaO) obtained in Clause 12.2.2.3 or 12.2.3.5.

12.4 Determination of sulfate

12.4.1 Reagents

- Dilute hydrochloric acid – Approximately 1:2 by v/v volume;
- Barium chloride solution – Approximately 10 % m/v.

12.4.2 Procedure

Weigh accurately about 2 g of the material and transfer it to a small beaker. Stir with 10 mL of cold water until all lumps are broken up and the lighter particles are in suspension. Add 15 mL of dilute hydrochloric acid and heat until reaction ceases. Filter and wash thoroughly with hot water. Dilute the filtrate to 250 mL, heat to boiling and add to it 10 mL of boiling barium chloride solution drop by drop with constant stirring. Boil for half an hour and allow to stand for four hours. Filter through a tarred sintered glass crucible, (No. 4). Wash the precipitate thoroughly with hot water until free from chlorides and dry to constant mass at 105 °C to 110 °C.

12.4.3 Calculation

Sulfates (as SO₄) percent by mass

$$= \frac{41.15 m_1}{m}$$

where,

m_1 represents mass in g of the barium sulfate precipitate; and
 m represents mass in g of the material taken for the test.

13. Determination of magnesium oxide

13.1 Methods

Two methods are described:

- (a) Method A is the classical method, and
- (b) Method B is the complexometric method.
- (c) However, in case of dispute, method A shall be followed.

13.2 Method A

13.2.1 Reagents

- (a) Dilute hydrochloric acid – Approximately 4 M.
- (b) Dilute ammonium hydroxide – Approximately 1:2 by volume.
- (c) Diammonium hydrogen phosphate – Solution same as in Clause 12.2.2.1.
- (d) Rectified spirit.

13.2.2 Procedure

Acidify the filtrate set apart from Clause 12.2.2.2 (or combined filtrates, in case of magnesium lime, see Clause 12.2.2.3) with dilute hydrochloric acid and evaporate until the salt begin to crystallize. Dilute until the salts are again in solution. Add a volume of dilute ammonium hydroxide equal to a third of the solution. Chill the solution and add slowly, with constant stirring 10 mL of Diammonium hydrogen phosphate solution. Let it stand until the precipitation is complete. Four hours are usually sufficient, but if possible, it is best to let the solution stand overnight. If the analysis is urgent, stir for half an hour and the precipitation will be complete. Filter through a weighed sintered crucible (previously ignited) and wash with a mixture of 1 part dilute aqueous ammonia solution, 1-part rectified spirit and 3 parts waters. Dry at 105 °C in an air oven, char the filter paper by gentle heating over a low flame and then slowly increase the flame and finish by heating at 900 °C to 950 °C till the precipitate is almost white, indicating that the salt has been converted to magnesium pyrophosphate. Cool in a desiccator and weigh.

13.2.3 Calculation

Magnesium oxide (as MgO), percent by mass

$$= \frac{181.2 m_1}{m_2}$$

where,

- m_1 represents mass in g of magnesium pyrophosphate; and
- m_2 represents mass in g of the material taken for the test in clause 10.2.1.

13.3 Method B

13.3.1 Reagents

- (a) Buffer solution – Same as in clause 12.2.3.1 (f).
- (b) Eriochrome black T indicator – Same as given in Clause 23.2.3.1 (d).

- (c) Standard disodium ethylene diamine tetra-acetate (EDTA) solution – Same as given in Clause 12.2.3.1. (b).

13.3.2 Procedure

Pipette out 10 mL of the prepared sample solution (see Clause 12.2.3.3) in a 250 mL conical flask and dilute with 35 mL of water. Add 5 mL of buffer solution and 5 drops of eriochrome black T indicator. Titrate against standard EDTA solution till the wine-red colour of the solution changes to blue.

13.3.3 Calculation

Magnesium oxide (as MgO), percent by mass

$$= \frac{7.190 (V_2 m_2 - V_1 m_1)}{m_3}$$

where,

V_2 represents the volume in mL of standard EDTA solution used in Clause 13.3.2;

m_2 represents mass in g of calcium oxide equivalent to one millilitre of standard EDTA solution as obtained in Clause 12.2.3.2 (b);

V_1 represents the volume in mL of standard EDTA solution used in Clause 12.2.3.4;

m_1 represents mass in g of calcium oxide equivalent to one millilitre of standard EDTA solution as obtained in Clause 12.2.3.2 (a);

m_3 represents mass in g of the barium sulfate precipitate obtained from the material;

14. Determination of sulfur

14.1 Principle

The total sulfur present is oxidized to sulfate and precipitated in the form of barium sulfate by the addition of barium chloride to a solution of the sample in hydrochloric acid. The suspension is filtered and the residual barium sulfate is washed and weighed. The concentration of total sulfur in the sample is calculated from the mass of barium sulfate produced.

14.2 Reagents

14.2.1 *Bromine*, ultra-pure.

14.2.2 *Bromine water*. Dissolve (1.0 ± 0.1) mL of ultra-pure bromine (14.2.1) in 24 mL of water. Store in the dark in a glass bottle. Renew this solution monthly.

14.2.3 *Barium chloride*, BaCl₂·2H₂O.

14.2.4 *Hydrochloric acid*, concentrated.

14.2.5 *Barium chloride solution*, 100 g/l. Dissolve 10.0 g of barium chloride (14.2.3) in 60 mL of water. Add 1 mL of hydrochloric acid (14.2.4) and dilute to 100 mL with water. Renew this solution daily.

14.3 Apparatus

14.3.1 *Electrical hot plate or sand bath*, controlled at (105 ± 5) °C.

14.3.2 *Filter paper*, medium, with a particle retention of 8 m.

14.3.3 *Filter paper*, fine ash less, with a particle retention of 2.5 °C.

14.3.4 *Crucible*, platinum or silica.

14.3.5 *Furnace*, controlled at (1 200 ± 50) °C.

14.4 Procedure

Take approximately 5 g of sample, weigh it to an accuracy of 0.001 g and transfer it to a 400 mL conical flask. Cover with a watch glass and carefully add 5 mL of bromine water (14.2.2) and 25 mL of hydrochloric acid (14.2.4). When the reaction has subsided, transfer the flask to the hot plate (14.3.1), evaporate to dryness and continue heating for 1 h at (105 ± 5) °C. Cool the flask

and contents, add 20 mL of hydrochloric acid (14.2.4) and concentrate the solution to approximately 10 mL by further heating.

Remove from the hotplate and wash off the watch glass with hot water (>60 °C) into the flask, adding hot water to give a final volume of approximately 80 mL. Bring to the boil, remove from the heat and allow the insoluble residue to settle for 3 min. Filter through a medium filter paper (14.3.2), collecting the filtrate in a 250 mL conical flask.

Transfer the residue from the conical flask to the filter paper and thoroughly wash with repeated portions of hot water to remove dissolved chlorides, draining between washes. Discard the filter paper and residue.

Add 2 mL of hydrochloric acid (14.2.4) to the filtrate and bring to the boil. Add 10 mL of barium chloride solution (14.2.5) and continue boiling for 20 min. Remove from the heat and stand the flask in a warm place overnight. Filter through the fine filter paper (14.3.3) and wash thoroughly with several portions of hot water, draining between washes. Transfer the filter paper and residue to a tared platinum or silica crucible (14.3.4). Place the crucible over a Bunsen burner or on a hotplate and char the paper without flaming. Place the crucible with charred paper and residue into the furnace (14.3.5) at $(1\ 200 \pm 50)$ °C for 20 min. Cool in a desiccator and weigh.

14.5 Calculation of results

Calculate the amount of sulfur present, S_1 as a percentage from the equation:

$$S_1 = \frac{13.7 m_2}{m_1}$$

Where;

m_1 is the mass of sample, in grams (g);

m_2 is the mass of the final residue, in grams (g).

15 Determination of Phosphorus

15.1 Principle

Phosphorus is precipitated as ammonium phosphomolybdate which is then reacted with standard sodium hydroxide solution, the excess of which is titrated with standard hydrochloric acid.

15.2 Reagents

- Dilute nitric acid – 1:1 (v/v).
- Sodium carbonate.
- Concentrated hydrochloric acid.
- Potassium permanganate solution – 1.5 % (m/v).
- Sodium sulfite – Solid.
- Dilute ammonium hydroxide solution – 1:1 (v/v).
- Concentrated nitric acid.
- Ammonium molybdate solution – Dissolve 100 g of molybdic anhydride in a mixture of 150 mL of water. Pour the solution slowly with constant stirring into a cold mixture of 480 mL of concentrated nitric acid and 100 mL of water. Stand the mixture for 24 h. Filter the solution before use.
- Potassium nitrate solution – 1 % (m/v) neutral to methyl orange.
- Methyl orange indicator solution – Dissolve 0.01 g of methyl orange in 100 mL of water.
- Phenolphthalein indicator solution – Dissolve 0.1 g of phenolphthalein in 100 mL of 60 % rectified spirit.
- Standard sodium hydroxide solution – 0.1 M.

(m) Standard hydrochloric acid – 0.1 M.

15.3 Procedure

Dissolve 10 g of the material in 80 mL of dilute nitric acid, filter and wash the residue with hot water. Take the residue in a platinum crucible, mix it with about 5 g of sodium carbonate, and ignite till the whole mass is fused. Cool, dissolve in dilute nitric acid and mix the solution with the main filtrate. Add 10 mL of concentrated hydrochloric acid and boil for half an hour. Filter off the silica. Oxidize the solution by boiling with 10 mL of potassium permanganate solution until a precipitate is formed. Dissolve the precipitate by the addition of a little sodium sulfite and boil to expel oxides of nitrogen and sulfur. Cool and just neutralize the solution with dilute ammonium hydroxide solution, and then add 1 mL of concentrated nitric acid. Heat the solution to 40 °C; add 50 mL of ammonium molybdate solution with constant stirring until the precipitate is formed. Allow the precipitate to stand for 1 h at 40 °C. Filter the yellow precipitate through a filter paper pad, wash several times with potassium nitrate solution till the washings are neutral to methyl orange indicator solution. Return the precipitate with the pad to the beaker in which the precipitation was carried out. Add 25 mL of water, 3 drops of phenolphthalein indicator solution a known volume of excess of standard sodium hydroxide solution and shake until the precipitate is dissolved. Titrate the excess of alkali against standard hydrochloric acid to the disappearance of the pink colour.

NOTE: Occasionally for the quantitative removal of silica, repeat dehydration and Baking at 110 °C to 115 °C may be necessary.

15.4 Calculation

Phosphorus (as P), percent by mass

$$\frac{0.0135(v_1 - v_2)}{m}$$

where,

v_1 represents the volume in mL of sodium hydroxide solution standard added;

v_2 represents the volume in mL of standard hydrochloric acid required to titrate the excess of alkali; and

m represents mass of the material taken for the test.

16 Determination of Manganese

16.1 Principle

The manganese present in the sample is converted by potassium periodate into the strongly coloured permanganate ion. After the intensity of the colour is measured, it is decomposed with sodium nitrite and an optical density of the colourless solution is measured.

16.2 Apparatus

Spectrophotometer with a 40 mm cell and wavelength of 520 nm to 525 nm.

16.3 Reagents

16.3.1 Stock test solution

Weigh approximately 5 g of the sample to an accuracy of 0.0001 g and ignite in a clean platinum crucible to 575 °C ± 25 °C.

Cool and transfer to a 400 mL tall beaker. Add 25 mL of water and 25 mL of perchloric acid ($\rho = 1.13$ g/L). Evaporate slowly on a hot plate until copious fumes of perchloric acid are evolved, cover with a watch glass and reflux for 10 min.

Cool the solution, dilute with four to five times its volume of water, heat to boiling and filter through loosely packed ash less paper pad using a rubber capped glass rod to remove any silica adhering to the sides of the beaker. Thoroughly wash with about 50 mL of hydrochloric acid (1+99) and finally with hot water until the filtrate is free from chloride.

16.3.2 Manganese, standard working solution

Dissolve 0.1000 g manganese metal in 10 mL concentrated hydrochloric acid mixed with one millilitre of nitric acid. Dilute to 1000 mL with water; 1.00 mL \equiv 100 μ g Mn.

16.4 Procedure

Pipette a 50 mL aliquot of the stock test solution into a 250 mL beaker, add 25 mL of phosphoric acid solution and 0.5 g of potassium periodate. Heat to boiling and simmer gently until the pink manganese colour begins to develop. Continue to simmer for 3 to 4 min, cool and dilute to 100 mL in a volumetric flask.

Measure the intensity of colour obtained in the solution in a spectrophotometer with a 40 mm cell, at a wavelength of 250 nm to 525 nm.

Add two drops of 2% (m/v) sodium nitrite solution by using pipette, swirl until decolourised and measure the optical density. The difference between the two readings is equivalent to the amount of manganese present.

16.5 Calibration of apparatus

To a series of 250 mL beakers, add from a burette a range of volumes of 0 mL to 30 mL of the standard manganese working solution. Treat them as described in 16.4 and construct a calibration curve by plotting the amount of manganese, in μ g, against optical density.

16.6 Expression of results

Obtain the amount of manganese from the calibration and then convert to the amount present in the original sample.

$$\text{Percentage manganese (as Mn)} = \frac{0.05 v}{m}$$

$$\text{Percentage manganese (as Mn)} = \frac{0.0719 v}{m}$$

where,

v = the equivalent volume of standard manganese working solution (mL);

m = the mass of the sample (g).

17 Determination of Carbon dioxide

17.1 Principle

Carbon dioxide is liberated from the sample by means of hydrochloric acid and absorbed in barium hydroxide solution. Phenolphthalein indicator is added to the resulting precipitate and the excess

alkalinity removed by hydrochloric acid. This is followed by a further titration with hydrochloric acid using bromophenol blue as indicator and the carbon dioxide content calculated from the volume of acid used.

17.2 Reagents

17.2.1 Barium chloride, BaCl₂.2H₂O.

17.2.2 Sodium hydroxide solution, approximately 1.0 M.

17.2.3 Barium hydroxide solution. Dissolve 125 g of barium chloride (17.2.1) in 1 L of water. Add 1 l of this solution to 1 L of sodium hydroxide solution (17.2.2) and mix in an aspirator fitted with a soda-lime guard tube. Allow any slight precipitate to settle before use.

17.2.4 Hydrochloric acid solution, 1.0 M.

17.3 Apparatus

The apparatus required is shown in Figure 1 and consists of an 800 mL Kjeldahl flask (A), connected via a rubber stopper to funnel B, and to bottle C using glass tubing (with an internal diameter of approximately 5 mm) which is fitted with a rubber teat safety device (E). Bottle C is fitted with a thermometer (F) and is connected to a vacuum via tap D.

NOTE: All components should be suitable for the vacuum to which they are subjected.

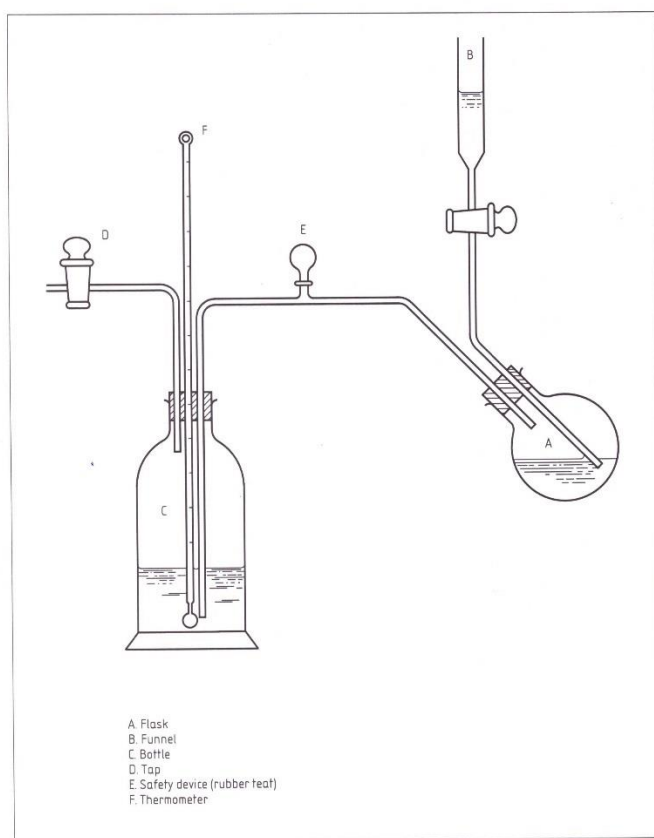


Figure 1 — Typical apparatus for determination of carbon dioxide

17.4 Procedure

Take one of the following masses of dry sample and weigh it to the nearest 0.1 g:

- 10 g quicklime;
- 10 g hydrated lime; or
- 1 g calcium carbonate.

Wash the sample into flask A, making sure that no particles adhere to the neck. Add water to give a total volume of approximately 100 mL. Assemble the apparatus, adding 40 mL of barium hydroxide solution (17.2.3) to bottle C, place a small amount of water in funnel B and evacuate through tap D to below 4 kPa. Close tap D and add 60 mL of hydrochloric acid (1 + 9) to funnel B. Carefully run the acid into flask A, taking care not to allow air into the apparatus, leaving 2 mL of the acid in the funnel. Close the tap of funnel B and add approximately 20 mL of water to act as a seal.

Heat flask A with a Bunsen burner while shaking bottle C continuously to assist the absorption of carbon dioxide. Continue heating until the temperature of bottle C reaches (70 ± 5) °C. Remove the burner and carefully open tap D. Remove bottle C, washing any precipitated barium carbonate from the delivery tube into the bottle. Add a few drops of phenolphthalein and neutralize exactly with hydrochloric acid, 1.0 M (17.2.4). Adjust the volume of barium hydroxide solution (17.2.3) added to flask A if necessary to ensure that there is an excess of barium hydroxide throughout the determination equivalent to a titration of at least 5 mL of hydrochloric acid, 1.0 M (17.2.4).

Add bromophenol blue and titrate the precipitated barium carbonate with hydrochloric acid, 1.0 M (17.2.4). Towards the end of the titration, stopper the bottle and shake the contents thoroughly after the addition of each portion of acid and continue until the end point is reached. Note the volume required in the second titration using bromophenol blue, X. Carry out blank determinations at frequent intervals.

17.5 Calculation of result

Calculate the amount of carbon dioxide as a percentage from the equation:

$$[CO_2] = \frac{2.2(X-Y)}{m}$$

Where;

m is the mass of sample, in grams (g);

X is the volume of acid required in the second titration, in millilitres (mL);

Y is the volume of acid required in the blank titration, in millilitres (mL).

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