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Abrasive grains and crude — Chemical analysis of fused aluminium oxide

Abrasifs en grains et en roche — Analyse chimique de l'oxyde d'aluminium électrofondu

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Contents

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 9285 was prepared by Technical Committee ISO/TC 29, *Small tools*, Subcommittee SC 5, *Grinding wheels and abrasives*.

Annex A of this International Standard is for information only.

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Abrasive grains and crude — Chemical analysis of fused aluminium oxide

1 Scope

This International Standard deals with the chemical analysis of abrasive grains or crude based on fused aluminium oxide. It applies to commercially available products but not necessarily to products which have been altered by use. It includes the following determinations:

- Loss on ignition
- Silicon dioxide
- Iron oxide
- Titanium dioxide
- Calcium oxide
- Magnesium oxide
- Zirconium oxide
- Aluminium oxide
- Analysis by atomic absorption spectrometry

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6353-1:1982, *Reagents for chemical analysis — Part 1: General test methods.*

ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series.*

ISO 6353-2/Add.2:1986, *Addendum 2 to ISO 6353-2:1983.*

ISO 6353-3:1987, *Reagents for chemical analysis — Part 3: Specifications — Second series.*

ISO 9138:1993, *Abrasive grains — Sampling and splitting.*

3 Reagents

3.1 General

Unless otherwise indicated, it is intended that all reagents shall conform to the specifications given in ISO 6353-1, ISO 6353-2 and ISO 6353-3. Other grades may be used, provided it be first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Unless otherwise indicated, references to water shall be understood to mean distilled water.

Paragraphs 3.2 to 3.21 include those reagents common to two or more analytical procedures. Other reagents will be found in the section which deals with the particular method in which they are used.

3.2 Concentrated acids and ammonium hydroxide.

Concentrated acids and ammonium hydroxide having the following approximate volumetric masses ρ, in grams per millilitre or concentrations, in percentage by mass will be required:

Hydrochloric acid (HCl): ρ = 1,18 g/ml
Nitric acid (HNO_3): ρ = 1,42 g/ml
Sulphuric acid (H_2SO_4): ρ = 1,84 g/ml
Hydrofluoric acid (HF): 40 % (m/m)
Phosphoric acid (H_3PO_4): 85 % (m/m)
Ammonium hydroxide (NH_4OH): ρ = 0,90 g/ml

3.3 Dilute acids and ammonium hydroxide.

The dilute acids and ammonium hydroxide referred to have varying concentrations. They shall be made up by mixing proportional volumes of the concentrated reagent and water. The dilute sulphuric acid mixtures shall be made up by slowly adding the acid to the water and stirring continuously. These dilutions are designated in the test procedures as (1 + 5), (1 + 8), etc., except for the very dilute solutions which are characterized by the percentage of reagent added. The designations in parentheses indicate the volume of the reagent added to the volume of water; for example H_2SO_4 (1 + 9) contains 10 % (V/V) of H_2SO_4 (ρ = 1,84 g/ml).

3.4 Ammonium acetate, 300 g/l solution.

Dissolve 300 g of $NH_4C_2H_3O_2$ in water. Fill to the 1 l mark with water.

3.5 Ammonium chloride (NH_4Cl).

3.6 Ammonium oxalate [$(NH_4)_2C_2O_4$], saturated solution.

3.7 Diammonium hydrophosphate, 100 g/l solution.

Dissolve 10 g of $(NH_4)_2HPO_4$ in 100 ml of water.

3.8 Barium diphenylamine sulphonate, 2 g/l solution.

Dissolve 0,5 g of the salt in 250 ml of H_2SO_4.

3.9 Hydrogen peroxide, 30 g/l solution.

3.10 Hydrogen sulfide gas (H_2S).

3.11 Hydroxylamine hydrochloride or hydroxylammonium chloride, 100 g/l solution.

Dissolve 50 g of $ClNH_3OH$ in 500 ml of water. Filter if necessary.

3.12 Mercuric chloride ($HgCl_2$), saturated solution.

3.13 Methyl red indicator, 1 g/l solution.

Dissolve 0,1 g methyl red in 100 ml of methanol.

3.14 *o*-Phenanthroline (1,10-phenanthroline), 1 g/l solution.

Dissolve 1 g *o*-phenanthroline monohydrate in 15 ml of ethanol (95 %). Dilute to 1 l with water.

3.15 Potassium dichromate ($K_2Cr_2O_7$), 0,01 mol/l solution.

Dissolve 2,942 4 g of $K_2Cr_2O_7$ in water. Make up the solution to the 1 l mark of a volumetric flask. Standardize the solution against a sample with a certified iron content.

3.16 Potassium permanganate ($KMnO_4$), standardized solution, c(1/5 $KMnO_4$) = 0,01 mol/l.

Dissolve 1,580 0 g of $KMnO_4$ in 500 ml of water. Allow to stand for 1 d-2 d. Filter through an asbestos mat and dilute to the 1 l mark of a volumetric flask with water. Standardize against sodium oxalate.

3.17 Potassium permanganate ($KMnO_4$), 50 g/l solution.

Dissolve 5 g $KMnO_4$ in 100 ml of water.

3.18 Potassium pyrosulfate ($K_2S_2O_7$).

3.19 Anhydrous sodium carbonate (Na_2CO_3).

3.20 Sodium tetraborate ($Na_2B_4O_7$).

3.21 Stannous chloride ($SnCl_2$), 50 g/l solution.

Dissolve 50 g of $SnCl_2$ in 100 ml of HCl. Make up to the 1 l mark of a volumetric flask with water. Store the solution with metallic tin in the bottle.

4 Apparatus

4.1 Small jaw or roll crusher with hardened steel faces.

4.2 Tool steel mortar.

In situations where it is vital that iron contamination be eliminated, the crushing should be carried out in a tungsten carbide mortar.

4.3 Sieve, with mesh of 150 µm aperture size.

4.4 Sieve, with 2 mm aperture size.

4.5 Platinum crucible, weighed, 30 ml, with lid.

5 Procedure

5.1 Preparation of samples for analysis

5.1.1 Abrasive crude

The sample, carefully obtained by means of an approved sampling method, is crushed in a small jaw or roll type crusher with hardened steel faces until it can be passed through a sieve having a mesh size of 2 mm; it is then mixed and divided by coning and quartering until approximately 500 g are obtained. The 500 g sample is in turn mixed and divided by coning and quartering until a sample weighing between 10 g and 20 g is obtained. This 20 g sample is then pulverized in a tool steel mortar until, unless otherwise specified, it completely passes through a sieve having a mesh size of 150 µm; it is then mixed thoroughly and placed in a container which will ensure freedom from contamination.

Precautions shall be taken in order to prevent the sample being contaminated by steel particles from the sampling and crushing equipment. Magnetic separation of the sample shall be carried out in order to remove this iron contamination.

5.1.2 Abrasive grain

The sample, carefully obtained by one of the approved methods, is thoroughly mixed and divided by coning and quartering until 10 g to 20 g are obtained. It is then crushed until, unless otherwise specified, it completely passes through a sieve having a mesh size of 150 µm; it is then carefully mixed and placed in a container which will ensure freedom from contamination (see ISO 9138).

5.2 Blank determination

Blank determination on the reagents shall be made for each determination and the necessary corrections applied in each case.

6 Gain or loss on ignition

6.1 Procedure

Weigh a 1 g sample to within 0,000 1 g and place it in a weighed platinum crucible which has been previously heated to 1 100 °C. Record the mass of the sample and the crucible. Heat the crucible plus sample at 1 100 °C until a constant mass is obtained. Cool the crucible in a desiccator and weigh the crucible plus sample.

6.2 Expression of results

Loss on ignition, expressed as a percentage, is given by the formula

$$\frac{(m_1 - m_2)}{m_0} \times 100$$

where

m_1 is the mass of the crucible plus sample before ignition, in grams;

m_2 is the mass of crucible plus sample after ignition, in grams;

m_0 is the mass of sample, in grams.

NOTE — If the sample gains in mass, report as a gain, and use the formula:

$$\frac{(m_2 - m_1)}{m_0} \times 100$$

7 Determination of silicon dioxide

7.1 Gravimetric method

7.1.1 Apparatus

7.1.1.1 Platinium crucible, with lid.

7.1.1.2 Beaker, 400 ml.

7.1.1.3 Filter paper, medium grade.

7.1.1.4 Desiccator.

7.1.2 Procedure

Weigh a 1 g sample to within 0,000 1 g and place in a platinum crucible containing 3 g of Na_2CO_3 and 3 g of $Na_2B_4O_7$. Mix the sample and fuse mixture thoroughly. Cover the crucible with a platinum lid and fuse the mixture at 1 000 °C until the entire sample is in solution. Rotate the crucible during cooling to deposit the melt in a thin layer on the side of the crucible. Place crucible and lid in a 400 ml beaker.

Dissolve the fusion in 100 ml of H_2SO_4 (1 + 4). When fully dissolved, thoroughly wash crucible and lid, adding washes to main solution.

Carefully evaporate the solution to fumes of SO_3 and leave to cool. Add 100 ml of water and boil to dissolve salts. Filter using a medium grade ashless filter paper. Wash the paper and precipitate with hot H_2SO_4 (2 + 98). Retain the filtrate for the Fe_2O_3, TiO_2, CaO and MgO determinations. Transfer the filter paper to a platinum crucible and char at low heat. When fully charred ignite at 1 000 °C. Leave the crucible to cool in a desiccator and weigh to constant mass.

Moisten the solid mass with 1 or 2 drops of water, add 10 ml of HF acid and 2 or 3 drops of H_2SO_4 (1 + 1). Slowly evaporate to dryness then ignite at 1 000 °C. Cool the crucible in a desiccator and weigh to constant mass. Evaluate the loss in mass due to HF, H_2SO_4 treatment.

7.1.3 Expression of results

Silicon dioxide content, expressed as a percentage by mass, is given by the equation

$$w(SiO_2) = \frac{m_1}{m_0} \times 100$$

where

m_1 is the mass loss due to the HF, H_2SO_4 treatment, in grams;

m_0 is the mass of the sample, in grams.

7.2 Colorimetric method

7.2.1 Reagents

7.2.1.1 Molybdic acid solution.

Dissolve 100 g of ammonium molybdate [82 % (*m/m*) of MoO_3] in approximately 600 ml of water. Add 70 ml of H_2SO_4 (ρ = 1,84 g/ml). Filter the solution. Dilute to 1 l with water in a volumetric flask.

7.2.1.2 Reducing solution.

Dissolve 25 g of sodium hydrogen sulphite ($NaHSO_3$) in 25 ml of water. Dissolve 2 g of sodium sulphite (Na_2SO_3) and 0,4 g of 1-amino-2-naphthol-4-sulphonic acid in 25 ml of water.

Mix the two solutions and dilute to 250 ml with water in a volumetric flask. Note that this solution has a maximum shelf life of two weeks.

7.2.1.3 Silicon dioxide, standard solution corresponding to 0,1 mg SiO_2 per millilitre.

Melt 0,100 g of anhydrous SiO_2 and 1 g of Na_2CO_3 in a platinum crucible. Cool the molten mass. Dissolve in water and make up to 1 000 ml in a volumetric flask. Transfer to a polyethylene bottle.

7.2.1.4 Tartaric acid, 100 g/l solution.

Dissolve 100 g of tartaric acid in water. Dilute to 1 000 ml in a volumetric flask.

7.2.1.5 Fusion mixture, comprising 3 parts Na_2CO_3 or 1 part B_2O_3. (Boric oxide is the preferred reagent. Salts containing boron have varying amounts of SiO_2 giving high and frequently inconsistent blank values.)

7.2.1.6 Hydrofluoric acid, 2 % (*V/V*) solution (for cleaning PTFE).

7.2.2 Apparatus

7.2.2.1 Platinum crucible.

7.2.2.2 PTFE beaker, 250 ml.

7.2.2.3 Magnetic stirrer.

7.2.2.4 PTFE stirring bar

7.2.2.5 pH-meter.

7.2.2.6 Volumetric flask, 100 ml.

7.2.2.7 Spectrophotometer.

7.2.3 Procedure

7.2.3.1 Sample size and dilutions

Use the table 1 to determine appropriate sample test portions and dilution.

7.2.3.2 Preparation of test solution

Weigh 5 g of fusion mixture into a 30 ml platinum crucible then weigh the appropriate size sample (see 7.2.3.1) into the crucible and cover with an additional 5 g of fusion mixture. Melt over a burner using platinum or nichrome triangles. Cool the melt to room temperature. Wash the outside of the crucible with water. Place the crucible in a

250 ml PTFE beaker and add enough water to cover the crucible. Bring to the boil until the melt is dissolved. Cool to room temperature and dilute to approximately 175 ml to 200 ml. Place the PTFE stirring bar in the beaker and place on a magnetic stirrer.

Using a pH-meter, adjust very carefully the pH of the solution to 1,8 using H_2SO_4 (1 + 1). **(Do not allow pH to go below 1,8.)**

If pH goes below 1,8 polymerization of the silicic acid starts to take place and polymerized silicic acid will not react to form silicomolybdic acid capable of being reduced to form the proper colour.

Transfer the solution to a volumetric flask (see 7.2.3.1 for flask size), dilute to the mark with water and mix.

Pipette an appropriate aliquot (see 7.2.3.1) into a 100 ml volumetric flask to which is added in the following order:

1) 2 ml of freshly prepared molybdic acid solution (see 7.2.1.1). Mix and allow to stand for 7 min;
2) 10 ml of tartaric acid solution (see 7.2.1.4);
3) 2 ml of reducing solution (see 7.2.1.2). Mix and allow to stand for 30 min.

Read absorbance at a wavelength of 700 nm, using 1 cm cells (for best accuracy, absorbance shall be in the range of 0,2 to 0,6).

Table 1

Assumed SiO_2 content %	Mass of test portion g	Dilution	Dilution factor d
0,1 to 0,5	1	250 ml – 25 ml	10
0,5 to 2,0	0,5	250 ml – 10 ml	25
1,0 to 5,0	0,2	250 ml – 10 ml	25
3,0 to 10,0	0,1	250 ml – 10 ml	25
10 to 20	0,1	500 ml – 10 ml	50
15 to 40	0,1	250 ml – 25 ml 250 ml – 2,5 ml	10 100

7.2.3.3 Preparation of calibration curve

Prepare a series of standard solutions to cover the expected range of silicon dioxide concentrations. Determine the absorbance of the solutions as described for the sample in 7.2.3.2. Prepare a calibration curve by plotting the absorbance values for the standard solutions against the concentration of SiO_2, in grams, per 100 ml of solution.

7.2.4 Expression of results

Silica content, expressed as a percentage by mass is given by the equation

$$w(\mathrm{SiO_2}) = \frac{m_1 \times d}{m_0} \times 100$$

where

d is the dilution factor (see 7.2.3.1);

m_1 is the mass, in grams, of silicon dioxide per 100 ml of sample solution as found by interpolation from the calibration curve;

m_0 is the mass of the sample, in grams.

8 Separation of iron, titanium, magnesium and calcium from aluminium

Evaporate the filtrate obtained from the gravimetric SiO_2 determination (see 7.1), or an aliquot of the solution from the colorimetric SiO_2 determination (see 7.2), until 150 ml to 200 ml of the solution is obtained. Adjust the acidity of the solution to nearly neutral with NaOH (550 g/l).

Add NaOH (550 g/l) dropwise until the precipitate just completely dissolves. Transfer the solution into a beaker containing 150 ml of cold NaOH (150 g/l) and 1 g of Na_2CO_3. Heat the solution and allow it to digest for one hour. Cool the solution. Filter the precipitate using a medium grade filter paper which has been treated with NaOH solution (150 g/l).

Wash with Na_2CO_3 (10 g/l). Dissolve the precipitate through the paper with 25 ml of hot HCl (1 + 9). Wash the paper with hot HCl (2 + 98). Dilute approximately 150 ml. Add 5 ml of H_2O_2 [3 % (*V*/*V*)]. Bring the solution to the boil. Add 1 g of ammonium chloride (NH_4Cl) and 3 drops of methyl red indicator solution. Add NH_4OH (1 + 1) dropwise until a persistent yellow colour is produced. Then add approximately 10 extra drops in excess. Bring the solution to the boil. Allow the solution to stand for one minute. Filter using a medium grade paper. Wash the paper and the precipitate with a hot ammonium chloride solution (NH_4Cl at 20 g/l) which has been made alkaline with NH_4OH.

Return the precipitate and the paper to the original beaker. Add 100 ml HCl (1 + 9). Stir until the precipitate has dissolved and the paper is completely macerated. Dilute to approximately 200 ml with water. Bring the solution to the boil.

Repeat both the precipitation with NH_4OH and the filtration. Combine the filtrates from the two precipitations and retain them for the CaO and MgO determinations. Dissolve the precipitate in 50 ml of H_2SO_4 (1 + 4). Transfer the solution to a 100 ml volumetric flask. Bring up to the mark with water.

9 Iron(III) oxide determination

9.1 Volumetric method

9.1.1 Apparatus

9.1.1.1 Filter paper, medium grade.

9.1.1.2 Beaker, 250 ml.

9.1.2 Procedure

Transfer a 50 ml aliquot of the mixed oxide solution prepared in 7.1.2 and treated as in clause 8 to a 250 ml beaker. Add 5 ml of HCl. Dilute to approximately 150 ml. Bring the solution to the boil and remove from heat. Pass a rapid stream of hydrogen sulphide (H_2S) through the solution for 30 min. Filter the solution through a medium grade paper. Wash the paper with HCl [1 % (*V*/*V*)] which has been previously saturated with H_2S. Evaporate the filtrate to approximately 100 ml. Add 10 ml of H_2O_2 [3 % (*V*/*V*)]. Boil the solution to remove excess H_2O_2. Add 10 ml HCl.

Oxidize the solution by adding $KMnO_4$ solution (100 g/l) dropwise until a persistent pink colour is obtained. Add $SnCl_2$ solution dropwise with continual stirring until the solution is colourless. Add one drop in excess. Cool the solution rapidly in a water bath. Add 15 ml of $HgCl_2$ solution. Allow the solution to stand for 3 min. Add 15 ml of H_3PO_4 (1 + 1), then 3 drops of barium diphenylamine sulphonate indicator solution.

Titrate with potassium dichromate until a persistent purple end point is obtained.

9.1.3 Expression of results

Iron(III) content expressed as a percentage by mass is given by the equation

$$w(Fe_2O_3) = \frac{V \times 7{,}984 \times c}{m_0} \times 100$$

where

V is the volume of potassium dichromate solution required, in millilitres;

c is the actual concentration of this solution, expressed in moles of potassium dichromate per litre;

m_0 is the mass of the sample, in grams.

9.2 Colorimetric method

9.2.1 Reagents

9.2.1.1 Standard iron solution, (1 ml $\hat{=}$ 1 mg Fe_2O_3).

Dissolve 4,91 g of ferrodiammonium disulphate $[Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O]$ in HCl (0,1 mol/l) or H_2SO_4 (0,05 mol/l), and dilute to the 1 l mark with the acid. Standardize the solution by titration against a solution of a standard oxidant.

9.2.1.2 Congo-red paper indicator.

9.2.1.3 1,10-Phenanthroline, 1 g/l solution.

9.2.2 Apparatus

9.2.2.1 Volumetric flask, 100 ml.

9.2.2.2 Beaker, 150 ml.

9.2.2.3 Hot plate.

9.2.3 Procedure

9.2.3.1 Preparation of test solution

Transfer a 25 ml aliquot of the mixed oxide solution (see clause 8) to a 150 ml beaker. Add 10 ml of hydroxylamine hydrochloride solution and 10 ml of tartaric acid solution (see 7.2.1.4). Add NH_4OH dropwise until the solution becomes alkaline to Congo-red paper. Add H_2SO_4 (1 + 1) dropwise until the solution just becomes acid to Congo-red paper. Add the ammonium acetate solution until the solution becomes alkaline again, then add 5 ml in excess. Add 10 ml of phenanthroline -1,10 solution. Transfer the solution to a 100 ml volumetric flask. Bring up to the mark with water.

Measure the absorbance of the solution using a wave length of approximately 500 nm. Use a blank test solution which has undergone all the successive procedures as a reference solution.

9.2.3.2 Preparation of calibration curve

Prepare a series of standard solutions to cover the expected range of iron oxide concentrations. Determine the absorbance as described for the sample solution in 9.2.3.1. Draw a calibration curve by plotting the absorbance values for the standard solution in terms of quantities, in milligrams, of Fe_2O_3 per 250 ml of solution.

9.2.4 Expression of results

From the measured absorbance of the sample solution, interpolate the amount of iron oxide in the sample solution from the calibration curve.

Iron(III) oxide content, expressed as a percentage by mass is given by the equation

$$w(Fe_2O_3) = \frac{m_1 \times V_1}{1\,000 \times V_0 \times m_0} \times 100$$

where

m_1 is the mass, in milligrams, of iron oxide per 250 ml of sample solution, as found by interpolation;

V_1 is the volume of mixed oxide solution, in millilitres;

V_0 is the volume of aliquot, in millilitres;

m_0 is the mass of the sample, in grams;

1 000 is the conversion factor, grams to milligrams.

10 Titanium dioxide colorimetric determination

10.1 Reagents

10.1.1 Titanium dioxide, standard solution.

Weigh 1,25 g of calcined TiO_2 and place in a platinum crucible. Fuse with 10 g of $K_2S_2O_7$, keeping the temperature as low as possible in order to maintain fluidity. Cool and dissolve in about 200 ml H_2SO_4 (1 + 1); cool. Transfer to a 1 000 ml volumetric flask. Dilute to the mark with water and mix thoroughly. Standardize the solution by precipitation with NH_4OH and ignition to TiO_2.

10.2 Apparatus

10.2.1 Platinum crucible.

10.2.2 Volumetric flask, 250 ml.

10.2.3 Volumetric flask, 1 000 ml.

10.3 Procedure

10.3.1 Preparation of test solution

Transfer a 50 ml aliquot of the mixed oxide solution (see clause 8) to a 250 ml volumetric flask. Add 50 ml of H_2SO_4 (1 + 1). Dilute the solution to approximately 200 ml. Add 5 ml of H_3PO_4 (1 + 1) and 5 ml of hydrogen peroxide [3 % (V/V) H_2O_2]. Dilute to the mark with water. Measure the absorbance of the solution using a wavelength of 425 nm. Use a blank reagent solution as a reference.

10.3.2 Preparation of calibration curve

Prepare a series of standard solutions to cover the expected range of titanium dioxide concentrations. Determine the absorbance of solution as described for the sample solution in 10.3.1. Draw a calibration curve by plotting the absorbance values for the standard solutions in terms of quantities (in milligrams) of TiO_2 per 250 ml of solution.

10.4 Expression of results

From the measured absorbance of the sample solution, interpolate the amount of titanium dioxide in the sample solution from the calibration curve (see 10.3.2).

Titanium dioxide content, expressed as a percentage by mass is given by the equation

$$w(\mathrm{TiO_2}) = \frac{m_1 \times V_1}{1\,000 \times V_0 \times m_0} \times 100$$

where

m_1 is the mass of titanium oxide, in milligrams, per 250 ml of sample solution, as found by interpolation;

V_1 is the volume of mixed oxide solution, in millilitres;

V_0 is the volume of aliquot, in millilitres;

m_0 is the mass of the sample, in grams;

1 000 is the conversion factor, grams to milligrams.

11 Calcium oxide gravimetric determination

11.1 Apparatus

11.1.1 Filter paper, fine grade.

11.1.2 Platinum crucible.

11.2 Procedure

Since manganese may be present in some materials and will interfere with the calcium and magnesium determinations it should be separated at this point.

Evaporate the filtrate obtained from the mixed oxide separation (see clause 8) to approximately 100 ml. Add 10 ml of saturated bromine water, make the solution alkaline with NH_4OH and add 15 drops in excess. Leave to digest until any manganese present precipitates as MnO_2, keeping the solution ammoniacal. Filter and wash with hot water.

Make the filtrate acidic by adding HCl to methyl red. Bring to the boil. Slowly add 10 ml of the ammonium oxalate solution. Add 5 ml of NH_4OH (1 + 1). Continue boiling the solution for 5 minutes. Allow the solution to digest overnight at a temperature slightly below the boiling point of the solution. Filter the precipitate on a fine paper. Wash the precipitate with the ammonium oxalate solution [0,1 % (m/m)] then dissolve the precipitate through the paper with 50 ml of HCl (1 + 4). Dilute the solution to approximately 100 ml. Precipitate and filter the calcium oxalate as above. Combine and retain the filtrates for the magnesium oxide determination.

Calcine the precipitate in a weighed platinum crucible at 1 000 °C until a constant mass is obtained. Weigh the precipitate as CaO.

11.3 Expression of results

Calcium oxide content, expressed as a percentage by mass is given by the equation

$$w(\text{CaO}) = \frac{m_1}{m_0} \times 100$$

where

m_1 is the mass of the precipitate, in grams;

m_0 is the mass of the sample, in grams.

12 Magnesium oxide gravimetric determination

12.1 Apparatus

12.1.1 Platinum crucible.

12.1.2 Filter paper, medium grade.

12.1.3 Filter paper, fine grade.

12.2 Procedure

Take the filtrate from the CaO determination, (see clause 11) and make it strongly acidic with nitric acid (HNO_3). Evaporate the solution until dry.

Dissolve the residue in 200 ml of HCl (1 + 19). Filter the solution through a fine paper. Wash the paper with water. Make the solution alkaline by adding NH_4OH dropwise, then add 10 ml in excess. Then add 20 ml of the diammonium hydrophosphate solution (see 3.7). Stir the solution vigorously for 1 min to 2 min. Allow the solution to stand overnight. Collect the precipitate on a medium grade filter paper using a filter accelerator. Wash the precipitate with ammonium nitrate solution (NH_4NO_3, 2 + 98). Dissolve the precipitate through the paper with 50 ml hot HCl (1 + 4). Make the solution alkaline by adding NH_4OH dropwise, and add a further 5 ml in excess. Add 5 ml of the ammonium phosphate solution. Stir, leave to digest, filter and wash as above.

Transfer the paper to a weighed platinum crucible. Calcine the precipitate at 1 100 °C in an oxidizing atmosphere. Weigh the precipitate as $Mg_2P_2O_7$.

12.3 Expression of results

Magnesium oxide content, expressed as a percentage by mass is given by the equation

$$w(\text{MgO}) = \frac{m_1 \times (36{,}22)}{m_0}$$

where

m_1 is the mass of the precipitate, in grams;

m_0 is the mass of the sample, in grams.

13 Zirconium oxide gravimetric determination

13.1 Precipitation of zirconium phosphate

Used when the zirconia concentration is less than 1,5 % (*m*/*m*).

13.1.1 Apparatus

13.1.1.1 Filter paper, medium grade.

13.1.1.2 Platinum crucible.

13.1.1.3 Meker burner.

13.1.1.4 Hot plate.

13.1.2 Procedure

Weigh 0,5 g of sample into a 30 ml platinum crucible. Add 10 g of potassium pyrosulphate ($K_2S_2O_7$) to the crucible. Fuse the sample over a Meker burner until the Al_2O_3 is completely dissolved. Cool the molten mass. Dissolve the fusion in 100 ml of HCl (1 + 9) in a 250 ml beaker. Evaporate the solution until dry on a hot plate. Continue heating for 1 h at over 100 °C. Cool the beaker. Dissolve the solids in 100 ml of H_2SO_4 (1 + 10). Filter the solution through a medium filter paper. Wash the paper with hot water. Add 10 ml of H_2O_2 [3 % (*V*/*V*)] then add 20 ml of $(NH_4)_2HPO_4$ (see 3.7). Allow the solution to digest overnight at 60 °C to 80 °C. Filter the precipitate on a medium filter paper. Wash the precipitate six times with the NH_4NO_3 solution (10 g/l). Place the precipitate and filter paper into a weighed platinum crucible; carefully burn off the filter paper at 1 000 °C until a constant mass is obtained. Weigh the precipitate as zirconium pyrophosphate (ZrP_2O_7).

13.1.3 Expression of results

Zirconium oxide content, expressed as a percentage by mass is given by the equation

$$w\left(\mathrm{ZrO_2}\right)=\frac{m_1\times\left(46{,}47\right)}{m_0}$$

where

m_1 is the mass of ZrP_2O_7, in grams;

m_0 is the mass of the sample, in grams.

13.2 Zirconium oxide, mandelic acid precipitation

Used when the zirconia concentration is greater than 1,5 % (*m*/*m*).

13.2.1 Reagents

13.2.1.1 Mandelic acid (DL-phenylglycolic acid).

13.2.2 Apparatus

13.2.2.1 Platinum crucible.

13.2.2.2 Filter paper, fine grade.

13.2.2.3 Beaker, 400 ml.

13.2.2.4 Meker burner.

13.2.2.5 Platinum filter cone.

13.2.2.6 Hot plate.

13.2.3 Procedure

Weigh 0,5 g of sample into a 30 ml platinum crucible. Add 5 g of a (1 + 1) mixture of Na_2CO_3 and $Na_2B_4O_7$ to the crucible. Mix the sample and fusion mixture thoroughly. Fuse over a Meker burner until completely dissolved. Cool, then place the crucible in a 400 ml beaker and cover with HCl (1 + 9). Add 15 ml-20 ml of concentrated HCl and boil until the fusion is completely dissolved. Cool the solution slightly, then add NaOH (25 %) until a white precipitate forms.

Add 30 ml concentrated HCl and dilute the volume to the 250 ml mark. Boil the solution for 2 min to 3 min. Add 16 g-18 g mandelic acid carefully while boiling. Remove the beaker from the hot plate when foaming begins. Add paper pulp, mix well and allow the solution to digest on a warm hot plate until clear (1 h to 2 h). Add more pulp and filter by suction through a fine paper using a platinum filter cone. Keep the solution warm while filtering. Wash the paper thoroughly with a hot phenylglycolic acid solution (50 g of phenylglycolic acid per 1 l of 2 % HCl). Transfer the paper and precipitate to a weighed platinum crucible, carefully burn off the paper, and then calcine at 1 000 °C until a constant weight is obtained. Weight the precipitate as ZrO_2.

13.2.4 Expression of results

Zirconium oxide content, expressed as a percentage by mass is given by the equation

$$w\left(\mathrm{ZrO_2}\right)=\frac{m_1}{m_0}\times 100$$

where

m_1 is the mass of the precipitate, in grams;

m_0 is the mass of the sample, in grams.

14 Aluminium oxide

Calculations

Aluminium oxide content, expressed as a percentage by mass is given by the equation

$$w\left(\mathrm{Al_2O_3}\right)=100-(A+B+C+D+E+F+G+H)$$

where

A is the percentage by mass, loss on ignition

B is the percentage by mass SiO_2

C is the percentage by mass Fe_2O_3

D is the percentage by mass TiO_2

E is the percentage by mass CaO

F is the percentage by mass MgO

G is the percentage by mass ZrO_2

H is the percentage by mass (Na_2O + K_2O + Cr_2O_3), where applicable.

15 Analysis by atomic absorption spectrometry

15.1 Reagents

15.1.1 Fluoroboric acid (HBF_4) 48 % (m/m) to 50 % (m/m).

15.1.2 Flux ($Li_2B_4O_7$).

NOTE — It is important that the analyses of the fluxes be checked by atomic absorption spectroscopy to ensure that they meet the required purity levels for analytical purposes.

15.1.3 Lanthanum chloride solution.

Dissolve 75 g of $LaCl_3 \cdot 6H_2O$ or 35 g of La_2O_3 in 400 ml HCl (1 + 1) and dilute to 1 l with water.

15.2 Apparatus

15.2.1 Stirrer-hot plate.

15.2.2 Magnetic stirrer, 1,25 cm bar.

15.2.3 Platinum crucible, 35 ml [nonwetting Pt + 5 % (*m/m*) Au], high form with lid.

15.2.4 Atomic absorption spectrometer.

A separate calibration curve shall be made for each spectrometer reading. Each curve shall be checked periodically to ensure reproduction.

NOTE — There are many atomic absorption spectrometer instruments on the market today, each one having slightly different features which make it impossible to perfect universal analytical methods. For general adjustment of the instrument, the manufacturer's guidelines should be followed. The best results will be obtained on a microprocessor controlled instrument with autolinerization, auto-zero, and by the use of two or three standards.

15.2.5 Pipette, 25,00 ml capacity.

15.2.6 Pipette, 20,00 ml capacity.

15.2.7 Pipette, 10,00 ml capacity.

15.2.8 Beaker, 250 ml.

15.2.9 Volumetric flask, 200 ml.

15.3 Preparation of sample

Same process as in 5.1.1 and 5.1.2 except for alumina/zirconia materials. For better fusion, these samples should pass through a 75 µm mesh sieve.

15.4 Procedure

15.4.1 Calibration

Standard solutions are obtained from standard samples of known composition or from various components taken from spectrographically pure oxides, which are weighed, melted and dissolved as described in 15.4.2. These synthetic standards shall be prepared exactly as are the samples and shall contain the same quantities of fusion mixture, acid and main components. Calibration curves covering the probable concentration ranges of the various components may be prepared in order to assess the concentration of these components in unknown materials.

In order to obtain optimum precision, it is advisable to determine the unknown solutions by bracketing between two standards, one being slightly higher, the other slightly lower in concentration.

Always use a standard having a slightly lower concentration and one having a slightly higher concentration than that of the component to be determined in the unknown sample. Update the calibration curve or its slope as often as is required by the stability of the instrument or the flame.

The readings "standard-sampled-standard" shall be repeated two or three times and averages worked out from the results. This will assist in eliminating any stability and linearity problems regarding the instruments.