45

INTERNATIONAL STANDARD

ISO 5795-1

First edition
1988-12-15

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
ORGANISATION INTERNATIONALE DE NORMALISATION
МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Rubber compounding ingredients — Kaolin clay —

Part 1:
Methods of test (excluding tests in rubber)

Ingrédients de mélange du caoutchouc — Kaolins —

Partie 1: Méthodes d'essai (à l'exclusion des essais de caoutchouc)

Reference number
ISO 5795-1 : 1988 (E)

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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 5795-1 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products.*

ISO 5795 will consist of the following parts, under the general title *Rubber compounding ingredients — Kaolin clay:*

- *Part 1: Methods of test (excluding tests in rubber)*
- *Part 2: Rubber tests*
- *Part 3: Specifications*

Annexes A to F form an integral part of this part of ISO 5795.

Printed in Switzerland

Rubber compounding ingredients — Kaolin clay —

Part 1:
Methods of test (excluding tests in rubber)

WARNING — Clays are liable to contain free crystalline silica (quartz). To avoid any risk to health, the relevant local legal requirements for dust levels in the atmosphere should be complied with.

1 Scope

1.1 This part of ISO 5795 specifies methods for the determination of the main physical and chemical properties of naturally occurring kaolin clays (complex hydrated aluminium silicates) used for compounding dry rubber.

1.2 Untreated natural clays may be slightly acidic. To overcome the possible retarding effect of an acidic filler on rate of vulcanization, such clays may be chemically treated with acid-neutralizing materials (e.g. amines) during manufacture. Both untreated and treated natural clays are included in this part of ISO 5795.

1.3 Natural clays which have been surface-modified (e.g. by treatment with silane) to achieve superior reinforcement of rubber are not within the scope of this part of ISO 5795.

1.4 Synthetic aluminium silicates and calcined natural clays are outside the scope of this part of ISO 5795.

1.5 The test recipe and determination of vulcanization characteristics (tests of clay in rubber) will be described in ISO 5795-2[1].

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 5795. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 5795 are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 787-10 : 1981, *General methods of test for pigments and extenders — Part 10: Determination of density — Pyknometer method.*

ISO 842 : 1984, *Raw materials for paints and varnishes — Sampling.*

ISO 3262 : 1975, *Extenders for paints.*

3 Sampling

Sampling shall be carried out in accordance with ISO 842.

4 Methods (excluding tests in rubber)

See table 1.

Table 1 — Properties and corresponding methods of test

Property	Method of test
% Silicon [reported as silica (SiO_2)]	Annex A
% Aluminium [reported as alumina (Al_2O_3)]	Annex B
$\frac{SiO_2}{Al_2O_3}$ ratio	Annex F
% Particles less than 2 µm (by mass)	ISO 3262 : 1975, clause 9
% Particles less than 10 µm (by mass)	ISO 3262 : 1975, clause 9
Copper, total, mg/kg	Annex D
Manganese, total, mg/kg	Annex E
% Iron, total	Annex C
% Residue on 45 µm sieve	ISO 3262 : 1975, clause 8
% Residue on 125 µm sieve	ISO 3262 : 1975, clause 8
pH of aqueous suspension	ISO 3262 : 1975, clause 13
% Matter volatile at 105 °C	ISO 3262 : 1975, clause 10
% Loss on ignition at 1 000 °C (on dried sample)	ISO 3262 : 1975, clause 11
Density	ISO 787-10
Colour	ISO 3262 : 1975, clause 7

1) To be published.

Annex A
(normative)

Determination of silicon content — Molybdosilicate spectrometric method

A.1 Principle

Fusion of the sample with sodium carbonate. Determination of silicon still insoluble in acid ("insoluble silica") as the loss in mass when it is converted to volatile silicon tetrafluoride by hydrofluoric acid. Determination of "residual silica" (i.e. the silicon rendered acid-soluble by fusion) spectrometrically as silicomolybdate.

Total silicon is reported as SiO_2, but this does not imply the presence of any free silica (SiO_2) in the sample.

A.2 Determination of insoluble silica

A.2.1 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

WARNING — All recognized health and safety precautions shall be observed throughout the determination.

A.2.1.1 Sodium carbonate, anhydrous.

A.2.1.2 Ammonium molybdate, 80 g/dm³ solution.

Dissolve 8,0 g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] crystals in 80 cm³ of warm water, then dilute with water to 100 cm³ in a 100 cm³ measuring cylinder.

Store in a polyethylene bottle (A.2.2.1).

A.2.1.3 Ammonium iron(II) sulfate, 100 g/dm³ solution.

Dissolve 10 g of ammonium iron(II) sulfate [$(NH_4)_2SO_4.FeSO_4.6H_2O$] crystals in 60 cm³ of warm water and 0,2 cm³ of sulfuric acid (A.2.1.9). Dilute with water to 100 cm³ in a 100 cm³ measuring cylinder.

NOTE — Always prepare this reagent freshly.

A.2.1.4 Ammonium iron(III) sulfate, 0,1 g/dm³ solution [calculated as iron(III) oxide].

Dissolve 0,060 3 g of ammonium iron(III) sulfate [$NH_4Fe(SO_4)_2.12H_2O$] crystals in 60 cm³ of warm water containing 1 cm³ of the sulfuric acid (A.2.1.9), then dilute to 100 cm³ with water in a 100 cm³ measuring cylinder.

Store in a polyethylene bottle (A.2.2.1).

A.2.1.5 Hydrochloric acid, concentrated, 36 % (m/m), ϱ = 1,18 Mg/m³.

A.2.1.6 Hydrofluoric acid, 40 % (m/m).

A.2.1.7 Silver nitrate, 10 g/dm³ solution.

Dissolve 1,0 g of silver nitrate ($AgNO_3$) crystals in water and dilute to 100 cm³ with water in a 100 cm³ measuring cylinder.

Store in an amber glass bottle.

A.2.1.8 Sulfuric acid, 50 % (V/V) solution.

Cautiously, taking all necessary precautions, add 125 cm³ of sulfuric acid [98 % (m/m), ϱ = 1,84 Mg/m³] to 100 cm³ of water in a beaker, allow to cool, then dilute with water to 250 cm³ in a measuring cylinder.

Store in a polyethylene bottle (A.2.2.1).

A.2.1.9 Sulfuric acid, 20 % (V/V) solution.

Cautiously add 50 cm³ of sulfuric acid [98 % (m/m), ϱ = 1,84 Mg/m³] to 150 cm³ of water in a beaker, cool, then dilute with water to 250 cm³ in a measuring cylinder.

Store in a polyethylene bottle (A.2.2.1).

A.2.2 Apparatus

Ordinary laboratory apparatus and

A.2.2.1 Polyethylene bottles, screw-capped, 250 cm³ and 1 dm³ capacity.

A.2.2.2 Platinum crucibles, 20 cm³ capacity, with platinum lid and platinum stirring rod (length 50 mm).

A.2.2.3 Meker or similar burner, capable of reaching approximately 900 °C to fuse the sodium carbonate with the test portion (see A.2.3.2), and 1 100 °C for the subsequent ignition step (see A.2.3.3.4).

A.2.2.4 Visible light spectrometer, the wavelength of which can be adjusted between 400 nm and 800 nm.

A.2.2.5 Nickel beaker, 400 cm³ capacity.

A.2.3 Procedure

A.2.3.1 Test portion

Transfer approximately 1 g of the sample to a platinum crucible (A.2.2.2), previously weighed to the nearest 0,1 mg, then weigh the crucible and contents to the nearest 0,1 mg to obtain the mass of the test portion (m_0).

A.2.3.2 Preparation of test portion

Add 5 g of the sodium carbonate (A.2.1.1) in portions to the crucible, mixing thoroughly between additions with the platinum stirring rod (see A.2.2.2), reserving about 0,5 g to cover the mixture. Place the lid on the crucible, then cautiously heat over the burner (A.2.2.3) until the crucible contents are molten. Maintain in the molten state for 30 min, then allow to cool.

A.2.3.3 Determination

A.2.3.3.1 Place the crucible and lid in a 600 cm^3 beaker, add 50 cm^3 of hot water, cover with a watch glass, then carefully add 30 cm^3 of the hydrochloric acid (A.2.1.5). Place the beaker on a low-temperature hot-plate (85 °C ± 5 °C) until the fusion cake becomes detached from the crucible. Remove the crucible from the beaker, rinse the contents of the crucible into the beaker with a jet of hot water, and remove adherent particles by rubbing with a rubber-tipped glass rod. Remove the crucible lid and clean in a similar fashion.

A.2.3.3.2 Evaporate the contents of the beaker to dryness on the low-temperature hot-plate, then place in an oven at 105 °C ± 5 °C for 1 h.

A.2.3.3.3 Allow the beaker to cool, then drench the residue with 10 cm^3 of the hydrochloric acid and dilute with 90 cm^3 of hot water. Warm to dissolve soluble salts, then filter through a 12,5 cm diameter medium-grade ashless filter paper (Whatman No. 40*), collecting the filtrate in a 500 cm^3 graduated flask. Wash the filter and beaker thoroughly with hot water, removing adherent particles from the beaker with a rubber-tipped glass rod. Continue washing until all chlorides have been removed from the filter paper and precipitate [test portions of the washings emerging from the funnel with a drop of the silver nitrate solution (A.2.1.7)].

Reserve the filtrate and washings (F_1).

A.2.3.3.4 Transfer the filter to the platinum crucible, previously weighed to the nearest 0,1 mg, wipe the inside of the beaker with a portion of dampened filter paper and place the latter in the crucible. Dry the crucible and contents in the oven at 105 °C ± 5 °C, then carefully ignite over the burner. When carbonaceous matter has been removed, complete the ignition at a temperature above 1 100 °C. Allow the crucible to cool in a desiccator, and weigh to the nearest 0,1 mg (m_1).

A.2.3.3.5 Moisten the silica residue with water, add 10 drops of the sulfuric acid solution (A.2.1.9), then 10 cm^3 of the hydrofluoric acid (A.2.1.6). Place the crucible on the hot-plate and evaporate to sulfuric acid fumes. Carefully expel residual sulfuric acid by cautious heating over the burner, then heat to about 1 000 °C for 5 min. Allow to cool in a desiccator and weigh to the nearest 0,1 mg (m_2).

A.2.4 Calculation of mass of insoluble silica

The mass of insoluble silica, m_3, in the test portion (A.2.3.1) is given, in grams, by the equation

$$m_3 = m_1 - m_2$$

where

m_1 is the mass, in grams, of the crucible and contents before treatment with hydrofluoric acid (see A.2.3.3.4);

m_2 is the mass, in grams, of the crucible and contents after treatment with hydrofluoric acid (see A.2.3.3.5).

A.3 Determination of residual silica

A.3.1 Reagents

A.3.1.1 Silica, standard stock solution corresponding to 1,000 g of SiO_2 per cubic decimetre (prepared from a quantity of high purity or precipitated silica which has been ignited at 1 100 °C to constant mass).

Fuse exactly 1,000 g (weighed to within 1 mg) of the ignited silica with 5 g of sodium carbonate (A.2.1.1) in a covered platinum crucible (A.2.2.2). Extract the fused cake in hot water after placing the crucible in the nickel beaker (A.2.2.5). Allow to cool and transfer the extract together with rinsings from the beaker and crucible to a 1 000 cm^3 one-mark volumetric flask and dilute to the mark with water.

Store in a polyethylene bottle (A.2.2.1).

1 cm^3 of this standard solution contains 1,000 mg of SiO_2.

A.3.1.2 Silica, standard solution corresponding to 50 mg of SiO_2 per cubic decimetre.

Transfer 50,0 cm^3 of the silica standard stock solution (A.3.1.1) to a 1 000 cm^3 one-mark volumetric flask and dilute to the mark with water.

1 cm^3 of this standard solution contains 50 µg of SiO_2.

A.3.1.3 Silica, standard solution corresponding to 10 mg of SiO_2 per cubic decimetre.

Transfer 50,0 cm^3 of the silica standard solution (A.3.1.2) to a 250 cm^3 volumetric flask and dilute to the mark with water.

1 cm^3 of this standard solution contains 10 µg of SiO_2.

*) Whatman No. 40 is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 5795 and does not constitute an endorsement by ISO of this product.

A.3.2 Calibration

A.3.2.1 To a series of six 100 cm^3 one-mark volumetric flasks, add 0 cm^3, 5,0 cm^3, 10,0 cm^3, 20,0 cm^3, 30,0 cm^3 and 35,0 cm^3 of the silica standard solution (A.3.1.3). The flasks will then contain 0 µg, 50 µg, 100 µg, 200 µg, 300 µg and 350 µg of silica (SiO_2), respectively.

A.3.2.2 Take each aliquot portion through the colour development procedure commencing at A.3.3.3, "To each flask, add 6 cm^3 of the ammonium iron(III) sulfate solution (A.2.1.4)...". It is not necessary to prepare a "B" solution for each concentration of silica, one being sufficient for the calibration series.

A.3.2.3 Measure the absorbance of each calibration solution as described in A.3.3.7.

A.3.2.4 Plot absorbance values against silica concentration, in micrograms per cubic decimetre, to obtain a calibration graph.

A.3.3 Determination

A.3.3.1 Fuse the residue in the crucible with 0,5 g of the sodium carbonate (A.2.1.1), allow to cool and extract with hot water generally as in A.2.3.2 and A.2.3.3.1. Carefully acidify by drop by drop addition of the hydrochloric acid (A.2.1.5), then combine the extract with the reserved filtrate (F_1) from A.2.3.3.3 and dilute to 500 cm^3 to form a combined diluted filtrate (F_2).

A.3.3.2 Transfer two 10 cm^3 aliquot portions of the combined diluted filtrate (F_2) from A.3.3.1 to two 100 cm^3 one-mark volumetric flasks (A and B).

NOTE — The blue molybdosilicate colour will be generated in A, while B will contain a compensating solution.

Retain the remaining combined filtrate (F_2) for use in the determinations described in annexes B and C.

A.3.3.3 To each flask, add 6 cm^3 of the ammonium iron(III) sulfate solution (A.2.1.4) and 1 cm^3 of the hydrochloric acid (A.2.1.5), then sufficient distilled water to bring the volume in each flask to 50 $cm^3 \pm 1$ cm^3.

A.3.3.4 To flask A, add 12 cm^3 of the sulfuric acid solution (A.2.1.8), then 10 cm^3 of the ammonium molybdate solution (A.2.1.2). Mix and allow to stand for 5 min.

A.3.3.5 To flask B, add 12 cm^3 of the sulfuric acid solution, then 10 cm^3 of the ammonium molybdate solution. Mix and allow to stand for 5 min.

A.3.3.6 To each flask, add 10 cm^3 of the ammonium iron(II) sulfate solution (A.2.1.3), dilute to 100 cm^3 immediately, mix and allow to stand for 5 min.

A.3.3.7 Measure the absorbance of the solution in flask A with reference to the solution in flask B in 10 mm path length cells in the spectrometer (A.2.2.4) at a wavelength corresponding to the maximum absorption (approximately 800 nm). Refer the value for absorbance to the calibration graph (A.3.2.3) to derive the mass of residual silica present in the aliquot portion taken for the determination (m_4).

A.3.4 Calculation of mass of residual silica

The mass of residual silica, m_5, in the test portion (A.2.3.1) is given, in grams, by the equation

$$m_5 = \frac{m_4 \times 50}{10^6}$$

where m_4 is the mass, in micrograms, of residual silica present in the aliquot portion taken for the determination (A.3.3).

A.4 Expression of results

The silicon content, expressed as a percentage by mass, as silica (SiO_2), is given by the formula

$$\frac{(m_3 + m_5) \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (A.2.3.1);

m_3 is the mass, in grams, of insoluble silica present in the test portion, calculated as in A.2.4;

m_5 is the mass, in grams, of residual silica present in the test portion, calculated as in A.3.4.

Annex B
(normative)

Determination of aluminium content — EDTA titrimetric method

B.1 Principle

Rendering aluminium acid-soluble by fusion with sodium carbonate. Removal of any iron by cupferron, followed by addition of EDTA to complex the aluminium. Back-titration of the excess EDTA with a standard zinc solution.

B.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

WARNING — All recognized health and safety precautions shall be observed throughout the determination.

B.2.1 Chloroform.

B.2.2 Ethanol (Ethyl alcohol).

B.2.3 Ammonia, concentrated solution, 35 % (m/m), ϱ = 0,880 Mg/m^3.

B.2.4 Ammonium acetate, buffer solution.

To 500 cm^3 of water, add 120 cm^3 of glacial acetic acid, stir, then add 74 cm^3 of the ammonia solution (B.2.3), with stirring. Allow to cool and dilute to 1 dm^3 in a measuring cylinder.

B.2.5 Cupferron, 60 g/dm^3 reagent solution.

Dissolve 6,0 g of cupferron [$C_6H_5N(NO)ONH_4$] in 50 cm^3 of water, then dilute to 100 cm^3 with water in a measuring cylinder. Filter free of any insoluble matter.

Prepare this reagent freshly.

B.2.6 Zinc, standard reference solution, $c(1/2\ Zn_2)$ = 0,05 mol/dm^3.

Dissolve 3,268 5 g of pure zinc chips in 15 cm^3 of the hydrochloric acid (A.2.1.5) in a 100 cm^3 beaker, transfer the solution to a 1 000 cm^3 one-mark volumetric flask and dilute to the mark with water.

B.2.7 Disodium ethylenediaminetetraacetate, standard volumetric solution, c(EDTA) ≈ 0,05 mol/dm^3.

B.2.7.1 Preparation

Dissolve 18,612 g of the disodium salt of ethylenediaminetetraacetic acid

$[CH_2N(CH_2COOH)CH_2COONa]_2.2H_2O$

in 800 cm^3 of water in a 1 000 cm^3 one-mark volumetric flask and dilute to the mark with water. Standardize against the zinc standard reference solution (B.2.6) as specified in B.2.7.2.

B.2.7.2 Standardization

Pipette 20,0 cm^3 of the EDTA solution (B.2.7.1) into a 500 cm^3 conical flask, add 4 drops of the bromophenol blue indicator solution (B.2.8) followed by the ammonium acetate buffer solution (B.2.4) until the indicator colour changes to blue from yellow. Add 10 cm^3 of the ammonium acetate buffer solution in excess. Dilute with water to approximately 100 cm^3, then add an equal volume of the ethanol (B.2.2). Add 1 cm^3 to 2 cm^3 of the dithizone solution (B.2.9) and titrate with the zinc standard solution (B.2.6) to a permanent pink end-point. Record the volume, in cubic centimetres, of titrant used (V_2).

B.2.7.3 Calculation of standardization factor

The factor which must be applied to the volume of EDTA disodium salt solution used in B.3.2 in order that it may be expressed as exactly 0,05 mol/dm^3 for the calculation (clause B.4) is given by the formula

$$\frac{V_1}{V_2}$$

where

V_1 is the volume, in cubic centimetres, of EDTA solution used in B.2.7.2 (= 20,0 cm^3);

V_2 is the volume, in cubic centimetres, of the zinc standard reference solution (B.2.6) used for the standardization.

B.2.8 Bromophenol blue, 1 g/dm^3 indicator solution.

Dissolve 0,10 g of bromophenol blue in 1,5 cm^3 of sodium hydroxide solution, c(NaOH) = 0,1 mol/dm^3, then dilute with water to 100 cm^3 in a measuring cylinder.

B.2.9 Dithizone, 0,25 g/dm³ indicator solution.

Dissolve 0,025 g of dithizone ($C_6H_5N_2CSNHNHC_6H_5$) in 80 cm³ of the ethanol (B.2.2).

B.3 Procedure

B.3.1 Transfer a 100 cm³ aliquot portion of the combined diluted filtrate (F_2 from A.3.3.1) to a 250 cm³ separating funnel, add 20 cm³ of the hydrochloric acid (A.2.1.5), mix the contents and allow to cool. Add 2 cm³ of the cupferron solution (B.2.5), mix, then extract the cupferrates by shaking with 20 cm³ of the chloroform (B.2.1) for 30 s. Allow the chloroform extract to separate, then run off and discard. Extract the solution with a further 20 cm³ of the chloroform, allow the layers to separate, then test the aqueous layer with 1 cm³ of the cupferron solution: if all cupferrates have been extracted, a transient white precipitate of the reagent will form. Continue extraction with fresh portions of chloroform until cupferrates and excess cupferron have been removed, as indicated by a water-white chloroform layer (excess cupferron imparts a green colour to chloroform). Discard all chloroform extracts.

B.3.2 Transfer the aqueous layer quantitatively to a 500 cm³ conical flask and heat to boiling to remove traces of chloroform. Allow to cool, add 4 drops of the bromophenol blue indicator solution (B.2.8), followed by careful addition of the ammonia solution (B.2.3) to change the indicator colour from yellow to blue. Immediately acidify by drop by drop addition of the hydrochloric acid (A.2.1.5), adding 4 to 6 drops excess. From a burette, dispense sufficient EDTA solution (B.2.7) to complex all aluminium present and provide at least 2 cm³ in excess. Note the volume, in cubic centimetres, of EDTA solution added (V_3). Add ammonium acetate buffer solution (B.2.4) until the bromophenol blue indicator colour changes from yellow to blue, then add 10 cm³ in excess. Heat the solution to boiling and boil for 10 min, then cool to room temperature.

B.3.3 Dilute the solution with an equal volume of the ethanol (B.2.2), add 1 cm³ to 2 cm³ of the dithizone solution (B.2.9) then titrate with the zinc standard reference solution (B.2.6) to a permanent pink end-point. Note the volume, in cubic centimetres, of the zinc standard reference solution used (V_4).

B.4 Expression of results

The aluminium content, expressed as a percentage by mass, as alumina (Al_2O_3), is given by the formula

$$\frac{(V_3 - V_4) \times 0{,}002\,55 \times 5 \times 100}{m_0}$$

$$= \frac{V_3 - V_4}{m_0} \times 1{,}275$$

where

V_3 is the volume, in cubic centimetres, of exactly 0,05 mol/dm³ EDTA disodium salt standard volumetric solution used in the titration of the aliquot portion of the test solution;

V_4 is the volume, in cubic centimetres, of the aliquot portion of the test solution;

m_0 is the mass, in grams, of the test portion (A.2.3.1);

0,002 55 is the mass, in grams, of alumina corresponding to 1,00 ml of EDTA solution, c(EDTA) = 0,050 mol/dm³.

Annex C
(normative)

Determination of total iron content — 2,2′-Bipyridyl spectrometric method

C.1 Principle

Rendering of any iron in the sample acid-soluble by fusion with sodium carbonate, followed by spectrometric determination of the total iron content with 2,2′-bipyridyl.

C.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

WARNING — All recognized health and safety precautions shall be observed throughout the determination.

C.2.1 Ammonium acetate, 200 g/dm³ solution.

Dissolve 200 g of ammonium acetate (CH_3COONH_4) in 600 cm³ of water, then dilute with water to 1 dm³ in a measuring cylinder.

C.2.2 2,2′-Bipyridyl, 2 g/dm³ solution.

Dissolve 0,2 g of 2,2′-bipyridyl [$(C_5H_4N)_2$] in 60 cm³ of water with gentle warming. Allow to cool and dilute with water to 100 cm³ in a measuring cylinder.

Use within 4 weeks of preparation.

C.2.3 Hydroxylammonium chloride, 500 g/dm³ solution.

Dissolve 50 g of hydroxylammonium chloride ($HONH_3Cl$) in 50 cm³ of water, then dilute with water to 100 cm³ in a measuring cylinder.

C.2.4 Iron, standard stock solution corresponding to 1,000 mg of Fe per cubic decimetre.

Dissolve 1,000 g ± 0,001 g of pure iron in a mixture of 10 cm³ of water and 5 cm³ of nitric acid (ϱ = 1,42 Mg/m³) in a 100 cm³ beaker. Boil to expel oxides of nitrogen. Allow to cool, transfer the solution to a 1 000 cm³ one-mark volumetric flask and dilute to the mark with water.

1 cm³ of this standard solution contains 1,000 µg of Fe.

C.2.5 Iron, standard solution corresponding to 50 mg of Fe per cubic decimetre.

Pipette 50,0 cm³ of the iron standard stock solution (C.2.4) into a 1 000 cm³ one-mark volumetric flask, add 10 cm³ of the hydrochloric acid (A.2.1.5) then dilute to the mark with water and mix.

1 cm³ of this standard solution contains 50 µg of Fe.

C.2.6 Iron, standard solution corresponding to 10 mg of Fe per cubic decimetre.

Pipette 50,0 ml of the iron standard solution (C.2.5) into a 250 cm³ one-mark volumetric flask, add 2,5 cm³ of the hydrochloric acid (A.2.1.5) then dilute to the mark with water and mix.

1 cm³ of this standard solution contains 10 µg of Fe.

C.3 Procedure

C.3.1 Preparation of test solution

C.3.1.1 Pipette a 20,0 cm³ aliquot portion of the combined diluted filtrate (F_2 from A.3.3.1) into a 50 cm³ one-mark volumetric flask.

C.3.1.2 Add 0,5 cm³ of the hydroxylammonium chloride solution (C.2.3), 2 cm³ of the 2,2′-bipyridyl solution (C.2.2) and 10 cm³ of the ammonium acetate solution (C.2.1), dilute to the mark with water and mix. Allow to stand for 10 min before carrying out the spectrometric measurements (C.4.1).

C.3.2 Preparation of calibration graph

C.3.2.1 To a series of six 50 cm³ one-mark volumetric flasks, add 0 cm³, 5,0 cm³, 10,0 cm³, 20,0 cm³, 25,0 cm³ and 30,0 cm³ of the iron standard solution (C.2.6). The flasks will then contain 0 µg, 50 µg, 100 µg, 200 µg, 250 µg and 300 µg of iron (Fe), respectively.

C.3.2.2 Take each standard matching solution through the colour development procedure (C.3.1.2).

C.3.2.3 Measure the absorbances of the solutions with reference to water in 10 mm path length cells, on the spectrometer (A.2.2.4) at a wavelength corresponding to the maximum absorption (approximately 520 nm).

C.3.2.4 Plot the absorbance values against the number of micrograms of iron in each flask to obtain a calibration graph.

C.4 Determination

C.4.1 Measure the absorbance of the solution obtained in C.3.1.2 with reference to water in 10 mm path length cells on the spectrometer (A.2.2.4), at a wavelength corresponding to the maximum absorption (approximately 520 nm).

C.4.2 Refer the absorbance value to the calibration curve (C.3.2.4) to derive the mass of iron present in the aliquot portion of the test solution (m_6).

C.4.3 If the absorbance is greater than the range covered by the calibration curve (C.3.2.4), repeat the determination using a smaller aliquot portion of the combined reserved filtrate (F_2 from A.3.3.1) and apply an appropriate factor in the calculation (clause C.5).

C.5 Expression of results

The total iron content, expressed as a percentage by mass, as iron(III) oxide (Fe_2O_3), is given by the formula

$$\frac{m_6 \times 1{,}43 \times 500}{m_0 V_5}$$

where

m_0 is the mass, in grams, of the test portion (A.2.3.1);

m_6 is the mass, in grams, of iron present in the aliquot portion of the test solution obtained from the calibration graph (see C.4.2);

V_5 is the volume, in cubic centimetres, of the aliquot portion of the test solution (C.3.1);

1,43 is the ratio of the relative molecular mass of Fe_2O_3 (= 159,68) to twice the relative atomic mass of Fe (= 111,68).

Annex D
(normative)

Determination of total copper content — Atomic absorption spectrometric method

D.1 Principle

Treatment with perchloric and hydrofluoric acids, which renders most clays soluble. Fusion of any still insoluble matter with sodium carbonate, and combination of the resulting fusion extract with the original acid extract to provide a complete solution. Determination of total copper content by atomic absorption spectrometry at 324,5 nm.

D.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

WARNING — All recognized health and safety precautions shall be observed throughout the determination.

D.2.1 Perchloric acid, 60 % (m/m).

D.2.2 Nitric acid, ϱ = 1,42 Mg/m^3.

D.2.3 Copper, standard stock solution corresponding to 1,000 g of Cu per cubic decimetre.

Dissolve 1,000 g ± 0,001 g of high purity copper metal chips in a mixture of 10 cm^3 of water and 5 cm^3 of the nitric acid (D.2.2) in a beaker. Boil to expel oxides of nitrogen. Allow to cool and dilute to the mark in a 1 000 cm^3 one-mark volumetric flask.

1 cm^3 of this standard solution contains 1,000 µg of Cu.

D.2.4 Copper, standard solution corresponding to 50 mg of Cu per cubic decimetre.

Pipette 50,0 cm^3 of the copper standard stock solution (D.2.3) into a 1 000 cm^3 one-mark volumetric flask, add 5 cm^3 of the nitric acid (D.2.2), then dilute to the mark with water and mix.

1 cm^3 of this standard solution contains 50 µg of Cu.

D.2.5 Copper, standard solution corresponding to 10 mg of Cu per cubic decimetre.

Pipette 50,0 cm^3 of the copper standard solution (D.2.4) into a 250 cm^3 one-mark volumetric flask, add 1 cm^3 of the nitric acid (D.2.2), then dilute to the mark with water and mix.

1 cm^3 of this standard solution contains 10 µg of Cu.

D.3 Apparatus

Ordinary laboratory apparatus and

D.3.1 Platinum dish, 50 cm^3 to 75 cm^3 capacity.

D.3.2 Atomic absorption spectrometer, with lamps.

D.4 Procedure

D.4.1 Test portion

Weigh, to the nearest 1 mg, approximately 2 g of the sample into the platinum dish (D.3.1).

D.4.2 Preparation of the test solution

D.4.2.1 Disperse with water (2 cm^3), add 5 cm^3 of perchloric acid (D.2.1) and 10 cm^3 of the hydrofluoric acid (A.2.1.6). Place the dish on a heated sand tray and evaporate to perchloric acid fumes. Remove from the sand tray and cool, add 10 cm^3 of the hydrofluoric acid, replace on the sand tray and evaporate the contents of the dish to dryness.

D.4.2.2 Treat the residue with 5 cm^3 of the perchloric acid (D.2.1), rinse the internal walls of the dish with 2 cm^3 of water, then evaporate to dryness on the sand tray.

D.4.2.3 Treat the residue with 5 cm^3 of the hydrochloric acid (A.2.1.5) and 20 cm^3 of water, then allow the mixture to digest on the heated sand tray until salts are in solution.

D.4.2.4 Filter through a Whatman No. 40*) medium-grade ashless filter paper, collecting the filtrate in a 100 cm^3 one-mark volumetric flask. Wash the dish and filter with hot water, collecting the washings in the volumetric flask, and reserve the filtrate plus washings (F_3). Place the filter in the platinum crucible (A.2.2.2), dry, then ignite over the burner (A.2.2.3). Fuse the residue with 0,5 g of the sodium carbonate (A.2.1.1), cool and treat with hot water. Acidify the solution by drop by drop addition of the hydrochloric acid (A.2.1.5), then combine with the reserved filtrate (F_3). Dilute to 100 cm^3 and mix. Transfer this test solution to a polyethylene bottle (A.2.2.1), and reserve some of the solution for the determination described in annex E.

*) Whatman No. 40 is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 5795 and does not constitute an endorsement by ISO of this product.

D.4.3 Preparation of calibration graph

D.4.3.1 To a series of six 50 cm^3 one-mark volumetric flasks, add by measuring pipette 0,5 cm^3, 2,5 cm^3, 5,0 cm^3, 10,0 cm^3, 15,0 cm^3 and 25,0 cm^3 of standard copper solution (D.2.5). Dilute each to 50,0 cm^3 with water and mix. The flasks will then contain solutions whose copper concentrations are 0,1 $\mu g/cm^3$, 0,5 $\mu g/cm^3$, 1,0 $\mu g/cm^3$, 2,0 $\mu g/cm^3$, 3,0 $\mu g/cm^3$ and 5,0 $\mu g/cm^3$, respectively.

D.4.3.2 Adjust the atomic absorption spectrometer (D.3.2) to measure copper at a wavelength of approximately 324,5 nm, using an air/acetylene flame, in accordance with the instrument manufacturer's instructions.

D.4.3.3 Aspirate the series of calibration solutions through the atomic absorption spectrometer, alternating each solution with water, and record the absorbance values.

D.4.3.4 Plot a calibration graph relating the absorbance values to the copper concentrations, in micrograms of copper per cubic centimetre, of the calibration solutions.

D.4.4 Determination

D.4.4.1 Aspirate the test solution alternately with water twice through the atomic absorption spectrometer as in D.4.3.3 and record the mean absorbance value.

D.4.4.2 Derive the copper concentration of the test solution, in micrograms per cubic centimetre, by relating its mean absorbance value to the calibration curve (D.4.3.4).

D.4.5 Blank test

Run a blank test through all stages of the above procedure, but omitting the test portion.

D.5 Expression of results

The total copper content, expressed in milligrams per kilogram, is given by the formula

$$\frac{\varrho(\mathrm{Cu})_1 - \varrho(\mathrm{Cu})_2}{m_7} \times 100$$

where

$\varrho(\mathrm{Cu})_1$ is the copper content, in micrograms per cubic centimetre, of the test solution;

$\varrho(\mathrm{Cu})_2$ is the copper content, in micrograms per cubic centimetre, of the blank test solution;

m_7 is the mass, in grams, of the test portion (D.4.1).