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Driers for paints and varnishes

Siccatifs pour peintures et vernis

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

This third edition cancels and replaces the second edition (ISO 4619:1998), which has been technically revised. The main changes compared to the previous edition are as follows:

- the concentration of phenolphthalein indicator solution in 7.7.2.6 has been reduced to 0,5 % following actual requirements;
- the determination of lead has been deleted;
- the normative references have been updated;
- the text has been editorially revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Driers for paints and varnishes

CAUTION — The procedures described in this document are intended to be carried out by qualified chemist or by other suitably trained and/or supervised personnel. The substances and procedures used in this document can be injurious to health if adequate precautions are not taken. It is the responsibility of the user of this document to establish appropriate health and safety practices prior to its use.

Attention is particularly drawn to the health hazards of heavy metals which might be a constituent of driers (e.g. cobalt, cerium, zirconium, vanadium).

1 Scope

This document specifies the requirements and the corresponding test methods for driers for paints, varnishes and related products. It applies to driers in the solid or liquid form. It does not apply to emulsifiable driers.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 150, *Raw, refined and boiled linseed oil for paints and varnishes — Specifications and methods of test*

ISO 1523, *Determination of flash point — Closed cup equilibrium method*

ISO 2592, *Petroleum and related products — Determination of flash and fire points — Cleveland open cup method*

ISO 2811-1, *Paints and varnishes — Determination of density — Part 1: Pycnometer method*

ISO 3251, *Paints, varnishes and plastics — Determination of non-volatile-matter content*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4618, *Paints and varnishes — Terms and definitions*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
drier
compound, usually a metallic soap, that is added to products drying by oxidation in order to accelerate this process

4 Descriptions

4.1 Solid driers

Solid driers are materials which can be manufactured in a hard, soft (highly viscous) or powder form.

4.2 Liquid driers

Liquid driers are materials which are supplied as solutions in organic solvents, usually white spirit.

All these types of driers, when dissolved in solvents (normally hydrocarbons), impart specific drying properties depending on the metal used.

4.3 Metals used

The following metals are normally used: cobalt, manganese, zinc, calcium, cerium (or other rare earths), iron, zirconium, vanadium, barium, aluminium, strontium, etc.

NOTE In this document, methods for determination of metal content are given only for those metals which are in common use.

4.4 Acids used

The following acids are used: fatty acids of linseed oils, tall-oil fatty acids, resinic acids, naphthenic acids, 2-ethylhexanoic acid, fatty iso-acids with 9 carbon atoms, other fatty acids with 9 to 11 carbon atoms, etc.

5 Requirements and test methods

5.1 Driers for paints shall conform to the requirements given in Table 1.

Table 1 — Requirements and test methods

Characteristic		Requirement	Test method	
			Solid driers	Liquid driers
Appearance		Clear and uniform; no suspended matter or sediment	7.1	8.1
Consistency, if required		As agreed between the interested parties	To be agreed between the interested parties	—
Colour		As agreed between the interested parties	7.2	8.2
Solubility (miscibility) in solvent, raw linseed oil and other drying media		No separation or deposit	7.3	8.3
Stability of solution		Clear solution; no clouding, gelation or sedimentation	7.4	8.4
Suspended solid matter	of liquid driers % (mass fraction)	max. 0,1	—	7.5
	of solid driers	As agreed between the interested parties	7.5	—

[a] Tolerance (absolute value) on the metal content declared or agreed.

Table 1 *(continued)*

Characteristic		Requirement	Test method	
			Solid driers	Liquid driers
Viscosity, only for liquid driers		As agreed between the interested parties	—	8.5
Volatile matter at 105 °C		As agreed between the interested parties	7.6	7.6
Flashpoint		As agreed between the interested parties	ISO 2592	ISO 1523
Density		As agreed between the interested parties	To be agreed between the interested parties	ISO 2811-1
Acidity or basicity		As agreed between the interested parties	7.7	7.7
Drying characteristics		As agreed between the interested parties	To be agreed between the interested parties	To be agreed between the interested parties
Metal content (range)	up to 10 % (mass fraction)	±0,2 % (mass fraction)[a]	Clause 9 or Clause 10	
	above 10 % (mass fraction) to 20 % (mass fraction)	±0,3 % (mass fraction)[a]		
	above 20 % (mass fraction) to 30 % (mass fraction)	±0,4 % (mass fraction)[a]		
	above 30 % (mass fraction)	±0,5 % (mass fraction)[a]		

[a] Tolerance (absolute value) on the metal content declared or agreed.

5.2 Driers named according to the commercial name of the main acid used shall contain at least 90 % of this acid, except for driers based on naphthenic acids, which shall contain at least 70 % of these acids, expressed as a percentage of the total mass of acid present.

NOTE The type and content of the acids can be determined by gas-chromatographic (GC) analysis, except in the case of naphthenic acids.

6 Sampling

Take a representative sample of the drier to be tested, as specified in ISO 15528.

7 Methods of test for solid driers

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity in accordance with ISO 3696.

7.1 Appearance and consistency

Examine the sample visually for uniformity. If the consistency is specified, a method for its determination shall be agreed between the interested parties.

7.2 Colour

Dissolve 1 part by mass of the drier in 1 part by mass of white spirit or other agreed solvent and compare the colour against an agreed sample or colour standard.

7.3 Solubility (miscibility) in solvents, raw linseed oil or other drying media

Slowly heat, raising the temperature at a rate of 1 °C/min, 5 g of the drier and 20 g of an agreed solvent (or drying medium) under reflux on a sand bath, with stirring, until a homogeneous solution is obtained.

Allow to cool to room temperature and examine the solution for clarity, clouding and any separation or deposit.

7.4 Stability of solution

Allow 3 portions of the solution obtained by the method specified in 7.3 to stand for 7 days in stoppered bottles, one at each of the following temperatures:

a) 0 °C;

b) ambient temperature;

c) 50 °C.

After 1 day and again after 7 days, examine the solutions for clarity, clouding sedimentation or gelation. The bottle used for the test at 50 °C shall be able to withstand the pressure generated.

7.5 Suspended solid matter

Weigh, to the nearest 0,1 g, 5 g of solid drier (or 10 g of liquid drier) into a glass flask and dissolve in (or dilute with) 100 g of white spirit or an agreed solvent. Stopper the flask, allow to stand at ambient temperature for 3 days, then filter off the sediment or suspended matter using a glass filter crucible of porosity P 16 (see ISO 4793). Wash the residue on the filter with the solvent and dry it at 105 °C for 3 h. Cool to ambient temperature and weigh to the nearest 1 mg.

Calculate the suspended solid matter SSM, as a percentage mass fraction, using Formula (1):

$$\mathrm{SSM} = \frac{m_1}{m_0} \times 100 \qquad (1)$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the residue.

7.6 Volatile matter

Proceed in accordance with ISO 3251, taking a flat-bottomed glass of aluminium dish and a test portion of (1,00 ± 0,02) g. Place the dish with the test portion in the air oven, maintained at (105 ± 2) °C. Leave it in the oven at this temperature for 3 h.

7.7 Acidity

7.7.1 Principle

A solution of the drier in toluene/propan-2-ol is passed through a strong acid cation exchanger and the total acid in the eluate is determined. From the total acid determined, the acid combined with the metal is subtracted.

If a negative value for the acidity is obtained, the drier tested is a basic drier.

The method is suitable for driers containing barium, calcium, cobalt or zinc as metals, but is not applicable to driers containing cerium, iron, manganese or zirconium as metals.

In such cases, the method shall be agreed between the interested parties.

7.7.2 Reagents

7.7.2.1 Cation exchanger: a strong-acid, ring-sulfonated polystyrene resin (for example, Merck 1, Dowex 50, Amberlite IR 120)[1].

7.7.2.2 Propan-2-ol.

7.7.2.3 Toluene.

7.7.2.4 Hydrochloric acid, approximately 5 % (mass fraction) solution.

7.7.2.5 Potassium hydroxide, approximately 0,2 mol/l standard volumetric solution in 96 % (volume fraction) ethanol.

7.7.2.6 Phenolphthalein, 0,5 % (mass fraction) solution in 96 % (volume fraction) ethanol.

7.7.3 Apparatus

Ordinary laboratory apparatus and glassware, and the following.

7.7.3.1 Suitable ion-exchange column, as shown in Figure 1, for instance.

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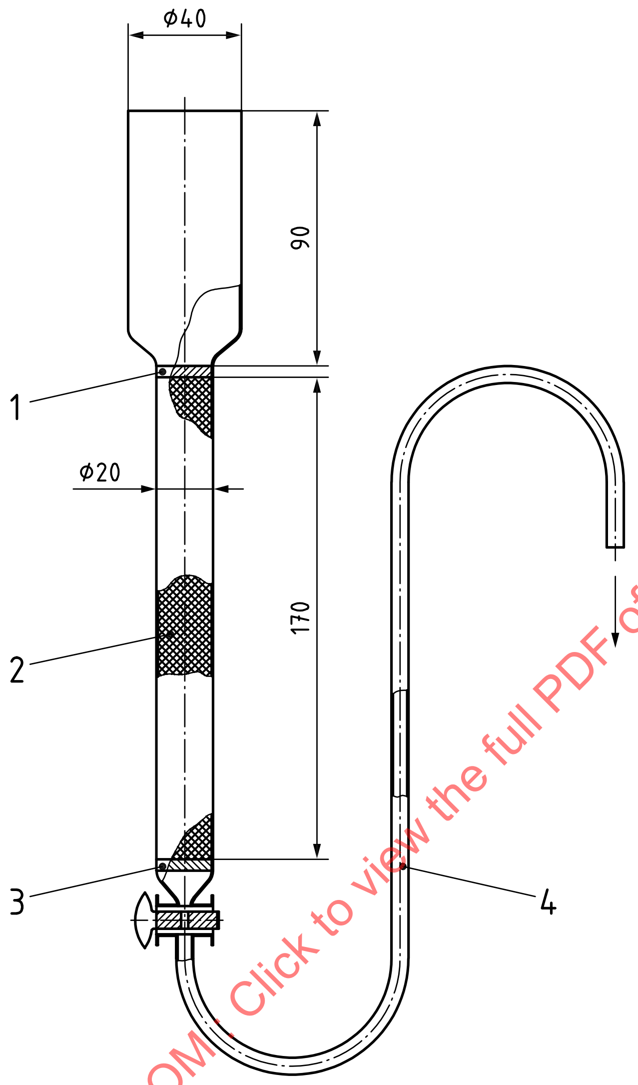
[1] These are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

Dimension in millimetres



Key

1	layer of glass wool
2	ion-exchange resin
3	sintered-glass disc
4	capillary tubing ⌀ 2 mm

Figure 1 — Example of a suitable ion-exchange column

7.7.4 Preparation of the ion-exchange column

Fill the ion-exchange column (7.7.3.1) with a quantity of the swollen ion-exchange resin (7.7.2.1) so that the height of resin in the column is about 170 mm. Pour 250 ml of the hydrochloric acid solution (7.7.2.4) gradually into the exchange column in order to change the resin into the hydrogen form. Drain off slowly, at about 1 or 2 drops per second (approx. 5 ml/min). When the acid has drained off completely, wash the resin successively with several 350 ml portions of water. The final washings shall not be acid to litmus paper. Then displace the water in the exchange column by 50 ml of propan-2-ol (7.7.2.2) and finally displace the propan-2-ol with 50 ml of a mixture (1 + 1) of propan-2-ol and toluene (7.7.2.3).

Do not use this column for more than about 50 milliequivalents of total metal.

7.7.5 Procedure

Weigh, to the nearest 1 mg, about 8 g of the drier to be tested into a 100 ml one-mark volumetric flask and dissolve in 50 ml of toluene (7.7.2.3). Dilute to the mark with propan-2-ol (7.7.2.2) and mix well. Pipette 25 ml of the solution into the ion-exchange column (7.7.4) and adjust the rate of flow to 5 ml/min. Collect the eluate in a 500 ml conical flask. When all the liquid has soaked through the resin, wash the exchange column with 150 ml of a mixture (1 + 1) of propan-2-ol and toluene, and collect the washings in the 500 ml conical flask, allowing them to drain off completely. Add a few drops of the phenolphthalein solution (7.7.2.6) to the eluate and titrate with the potassium hydroxide solution (7.7.2.5) to the end-point.

7.7.6 Expression of results

The acidity, expressed in milligrams of potassium hydroxide (KOH) per gram, is given by Formula (2):

$$\text{Acidity} = \left(\frac{4 \times V \times T}{m} - \frac{10 \times w \times n}{A} \right) \qquad (2)$$

where

V	is the volume, in millilitres, of the potassium hydroxide solution (7.7.2.5) required for the titration;
T	is the exact concentration of the potassium hydroxide solution (7.7.2.5), in moles of KOH per litre;
w	is the metal content, as a percentage mass fraction, of the drier, as determined in Clause 9;
n	is the valency of the metal in the drier;
m	is the mass, in grams, of the test portion;
A	is the relative atomic mass of the metal in the drier.

For mixed driers the factor $\frac{w \times n}{A}$ shall be calculated, taking into account the composition of the mixed drier.

8 Methods of test for liquid driers

8.1 Appearance

Examine the sample visually for uniformity, clarity, suspended matter or sediment.

8.2 Colour

Compare the colour of the liquid drier against that of an agreed sample or colour standard.

8.3 Solubility (miscibility) in solvents, raw linseed oil or other drying media

8.3.1 Prepare a mixture as follows:

Raw linseed oil, in accordance with ISO 150 (see 8.3.2):	16 parts by volume
Mineral solvents, e.g. white spirit with an aromatic content of approximately 25 % (volume fraction) (see 8.3.3):	4 parts by volume
The drier under test (at standard strength) (see 8.3.4):	1 part by volume

8.3.2 In the case of driers containing calcium, barium or rare earths, it is recommended that an air-drying alkyd resin [non-volatile content at least 60 % (mass fraction)] be used instead of linseed oil.

8.3.3 Allow the mixture to stand at room temperature for 6 h and then examine it for clarity, noting any clouding, separation or deposit.

8.3.4 The exact aromatic content of the solvent shall be agreed between the interested parties. For the purpose of this test, the standard strength of the drier is defined, in % (mass fraction), as

6	Co
6	Mn
8	Zn
4	Ca
6	Ce (or other rare earth)
6	Fe
6	Zr
12,5	Ba

Dilute driers of higher concentration than those above with mineral solvent until the standard strength is obtained.

8.4 Stability of solution

Prepare three mixtures of 10 g of liquid driers and 10 g of mineral solvent (the exact aromatic content of which shall be agreed between the interested parties), and allow to stand for 7 days in stoppered bottles, one at each of the following temperatures:

a) 0 °C;

b) ambient temperature;

c) 50 °C.

After this period, examine the solutions for clarity, noting any clouding, sedimentation or gelation. The bottle used for the test at 50 °C shall be able to withstand the pressure generated.

8.5 Viscosity

A suitable method shall be agreed between the interested parties, for example by the procedure specified in ISO 2431 (flow cup method), ISO 3219 (rotational viscometer working at known shear rate) or falling-ball methods.

9 Methods for determination of metal content of driers containing only one metal

9.1 General

During the analysis, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696. All indicator solutions should preferably be freshly prepared but shall in no case be older than 2 weeks.

NOTE The methods are not selective for only one metal. In case of doubt, a qualitative test for the presence of other metals can be carried out. Other methods, e.g. atomic absorption spectrometry (AAS), can be used by agreement between the interested parties.

9.2 Cobalt [ethylene diaminetetraacetic acid (EDTA) titrimetric method]

9.2.1 Reagents

9.2.1.1 Hydroxylammonium chloride ($OHNH_3Cl$).

9.2.1.2 Propan-2-ol.

9.2.1.3 Ethanol, 96 % (volume fraction) solution.

9.2.1.4 Hydrochloric acid, c(HCl) approximately 1 mol/l.

9.2.1.5 Hexamethylenetetramine, 40 % (mass fraction) aqueous solution.

9.2.1.6 EDTA, standard volumetric solution, 0,100 mol/l.

Dissolve 37,225 0 g of ethylene diaminetetraacetic acid (EDTA) dihydrate, disodium salt, in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix well.

Store the solution in a polyethylene bottle.

9.2.1.7 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution.

a) Preparation

Dissolve 14,38 g of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

b) Standardization

Pipette 20 ml of the zinc sulfate solution into a 250 ml conical flask. Dilute to about 100 ml with water and add successively 10 ml of buffer solution (9.2.1.8) and 5 or 6 drops of Mordant black 11 indicator solution (9.2.1.9). Titrate with EDTA solution (9.2.1.6) until the first change of the red colour to blue.

c) Calculation of concentration

The concentration T_1 of the zinc sulfate solution, in moles of $ZnSO_4$ per litre, is given by Formula (3):

$$T_1 = \frac{V_1 \times T_0}{20} \quad (3)$$

where

V_1 is the volume, in millilitres, of EDTA solution (9.2.1.6) required for the titration;

T_0 is the concentration of the EDTA solution (9.2.1.6), in moles of EDTA per litre.

9.2.1.8 **Buffer solution**, pH 10.

Add 54 g of ammonium chloride and 350 g of ammonia solution (ρ approximately 0,91 g/cm^3) to water in a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix well.

Store the solution in a polyethylene bottle.

9.2.1.9 **Mordant black 11[2] indicator solution**.

Dissolve 0,5 g of Mordant black 11 and 2,25 g of hydroxylammonium chloride (9.2.1.1) in 100 ml of ethanol (9.2.1.3).

9.2.1.10 **Xylenol orange/potassium nitrate mixture**, 1 + 100, for use as indicator.

9.2.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 120 mg of cobalt into a 250 ml conical flask. Add 25 ml of hydrochloric acid (9.2.1.4) and heat to boiling.

Dilute with 100 ml of propan-2-ol (9.2.1.2), add 15 ml of hexamethylenetetramine solution (9.2.1.5) and 0,050 g of xylenol orange/potassium nitrate mixture (9.2.1.10). Titrate with EDTA solution (9.2.1.6) until the violet colour just changes to yellow.

If desired, back-titrate with zinc sulfate solution (9.2.1.7) until the first change of the yellow colour to red.

9.2.3 Expression of results

The cobalt content, w_{Co}, expressed as a percentage mass fraction, is given by Formula (4):

$$w_{\mathrm{Co}} = \frac{\left[(V_2 \times T_0) - (V_3 \times T_1)\right] \times 0{,}058\,94}{m_2} \times 100$$

$$= \frac{(V_2 \times T_0) - (V_3 \times T_1)}{m_2} \times 5{,}894 \qquad (4)$$

where

V_2 is the volume, in millilitres, of EDTA solution (9.2.1.6) required;

V_3 is the volume, in millilitres, of zinc sulfate solution (9.2.1.7) required (if used);

T_0 is the concentration of the EDTA solution (9.2.1.6), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.2.1.7), in moles of $\mathrm{ZnSO_4}$ per litre;

m_2 is the mass, in grams, of the test portion.

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[2] Listed in Colour Index as C.I. 14645. Trade names include “Chrome Fast Black CAT, KIT & TS”, “Eriochrome Black DW, T and TDW”, “Potting Black C”. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

9.3 Manganese (EDTA titrimetric method)

9.3.1 Reagents

9.3.1.1 Ascorbic acid or hydroxylammonium chloride ($OHNH_3Cl$).

9.3.1.2 Toluene.

9.3.1.3 Propan-2-ol.

9.3.1.4 EDTA, 0,100 mol/l standard volumetric solution (see 9.2.1.6).

9.3.1.5 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.2.1.7).

9.3.1.6 Buffer solution, pH 10 (see 9.2.1.8).

9.3.1.7 Mordant black 11 indicator solution (see 9.2.1.9).

9.3.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 80 mg of manganese into a 250 ml conical flask. Dissolve the test portion in 10 ml of toluene (9.3.1.2) and dilute with 50 ml of propan-2-ol (9.3.1.3). Add approximately 0,100 g of ascorbic acid or hydroxylammonium chloride (9.3.1.1). Add successively 10 ml of buffer solution (9.3.1.6) and 5 or 6 drops of Mordant black 11 indicator solution (9.3.1.7). Titrate with EDTA solution (9.3.1.4) until the colour just changes from red to blue.

If desired, back titrate with zinc sulfate solution (9.3.1.5) until the first change of the blue colour to red.

9.3.3 Expression of results

The manganese content, w_{Mn}, expressed as a percentage mass fraction, is given by Formula (5):

$$w_{Mn} = \frac{\left[(V_4 \times T_0) - (V_5 \times T_1)\right] \times 0{,}054\,93}{m_3} \times 100$$

$$= \frac{(V_4 \times T_0) - (V_5 \times T_1)}{m_3} \times 5{,}493 \qquad (5)$$

where

V_4 is the volume, in millilitres, of EDTA solution (9.3.1.4) required;

V_5 is the volume, in millilitres, of zinc sulfate solution (9.3.1.5) required (if used);

T_0 is the concentration of the EDTA solution (9.3.1.4), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.3.1.5), in moles of $ZnSO_4$ per litre;

m_3 is the mass, in grams, of the test portion.

9.4 Zinc (EDTA titrimetric method)

9.4.1 Reagents

9.4.1.1 Toluene.

9.4.1.2 Propan-2-ol.

9.4.1.3 EDTA, 0,100 mol/l standard volumetric solution (see 9.2.1.6).

9.4.1.4 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.2.1.7).

9.4.1.5 Buffer solution, pH 10 (see 9.2.1.8).

9.4.1.6 Mordant black 11 indicator solution (see 9.2.1.9).

9.4.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 100 mg of zinc into a 250 ml conical flask. Dissolve the test portion in 10 ml of toluene (9.4.1.1) and dilute with 50 ml of propan-2-ol (9.4.1.2). Add successively 10 ml of buffer solution (9.4.1.5) and 5 or 6 drops of Mordant black 11 indicator solution (9.4.1.6). Titrate with EDTA solution (9.4.1.3) until the colour just changes from red to blue.

If desired, back-titrate with zinc sulfate solution (9.4.1.4) until the first change of the blue colour to red.

9.4.3 Expression of results

The zinc content, w_{Zn}, expressed as a percentage mass fraction, is given by Formula (7):

$$w_{Zn} = \frac{\left[(V_7 \times T_0) - (V_8 \times T_1)\right] \times 0{,}065\,38}{m_5} \times 100$$

$$= \frac{(V_7 \times T_0) - (V_8 \times T_1)}{m_5} \times 6{,}538 \qquad (7)$$

where

V_7 is the volume, in millilitres, of EDTA solution (9.4.1.3) required;

V_8 is the volume, in millilitres, of zinc sulfate solution (9.4.1.4) required (if used);

T_0 is the concentration of the EDTA solution (9.4.1.3), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.4.1.4), in moles of $ZnSO_4$ per litre;

m_5 is the mass, in grams, of the test portion.

9.5 Calcium (EDTA titrimetric method)

9.5.1 Reagents

9.5.1.1 Toluene.

9.5.1.2 Propan-2-ol.

9.5.1.3 Hydrochloric acid, c(HCl) approximately 4 mol/l.

9.5.1.4 EDTA, 0,100 mol/l standard volumetric solution (see 9.2.1.6).

9.5.1.5 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.2.1.7).

9.5.1.6 Buffer solution, pH 10 (see 9.2.1.8).

9.5.1.7 Mordant black 11 indicator solution (see 9.2.1.9).

9.5.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 60 mg of calcium into a 250 ml conical flask. Dissolve the test portion in 10 ml of toluene (9.5.1.1) and dilute with 50 ml of propan-2-ol (9.5.1.2). Add 3 ml of hydrochloric acid (9.5.1.3). Add successively 10 ml of buffer solution (9.5.1.6) and 5 or 6 drops of Mordant black 11 indicator solution (9.5.1.7). Titrate with EDTA solution (9.5.1.4) until the colour just changes from red to blue.

If desired, back-titrate with zinc sulfate solution (9.5.1.5) until the first change of the blue colour to red.

9.5.3 Expression of results

The calcium content, w_{Ca}, expressed as a percentage mass fraction, is given by Formula (8):

$$w_{\mathrm{Ca}} = \frac{\left[(V_9 \times T_0)-(V_{10} \times T_1)\right] \times 0{,}040\,8}{m_6} \times 100$$

$$= \frac{(V_9 \times T_0)-(V_{10} \times T_1)}{m_6} \times 4{,}008 \qquad (8)$$

where

V_9 is the volume, in millilitres, of EDTA solution (9.5.1.4) required;

V_{10} is the volume, in millilitres, of zinc sulfate solution (9.5.1.5) required (if used);

T_0 is the concentration of the EDTA solution (9.5.1.4), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.5.1.5), in moles of $ZnSO_4$ per litre;

m_6 is the mass, in grams, of the test portion.

9.6 Iron (Iodometric method)

The method is suitable for the determination of up to 0,200 g of iron. It is not applicable in the presence of oxidizing materials or anions which combine with iron(III) ions to give complexes.

9.6.1 Principle

The drier is hydrolysed by boiling in sulfuric acid/ethanol/toluene medium. Any iron(II) is oxidized with cerium(IV) sulfate using ferroin as indicator. Iron(III) is reduced by iodide as follows:

$$2Fe^{3+} + 2I^{-} \leftrightarrow 2Fe^{2+} + I_2$$

The liberated iodine is titrated with standard volumetric sodium thiosulfate solution. Iodide should be present in large excess to favour the reaction from left to right. The determination is carried out in a carbon dioxide atmosphere to prevent atmospheric oxidation of iodide.

9.6.2 Reagents

9.6.2.1 Sodium hydrogen carbonate.

9.6.2.2 Potassium iodide.

9.6.2.3 Toluene.

9.6.2.4 Ethanol, 96 % (volume fraction) solution.

9.6.2.5 Sulfuric acid, $c(H_2SO_4)$ approximately 2 mol/l.

9.6.2.6 Cerium(IV) sulfate, approximately 0,1 mol/l solution.

Weigh 65 g of cerium(IV) ammonium sulfate dihydrate $[Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O]$, or 33 g of cerium(IV) sulfate $[Ce(SO_4)_2]$, and dissolve in a mixture of 250 ml of water and 250 ml of sulfuric acid (9.6.2.5). Allow to stand for 48 h, filter through a sintered-glass filter crucible, porosity P 16 (see ISO 4793) and dilute to 1 000 ml.

9.6.2.7 Sodium thiosulfate, approximately 0,1 mol/l standard volumetric solution.

9.6.2.8 Ferroin, approximately 0,01 mol/l indicator solution.

Weigh 0,278 g of iron(II) sulfate heptahydrate $(FeSO_4 \cdot 7H_2O)$, dissolve in water and dilute to 80 ml. Dissolve 0,594 g of 1,10-phenanthroline monohydrate or 0,650 g of 1,10-phenanthroline hydrochloride in this solution, dilute to 100 ml and mix.

9.6.2.9 Starch, 5 g/l solution.

9.6.3 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 150 mg of iron into a 250 ml conical flask. Add 15 ml of toluene (9.6.2.3) and swirl until completely dissolved. Add successively 15 ml of ethanol (9.6.2.4) and 25 ml of sulfuric acid (9.6.2.5). Add some boiling aids, mount an air condenser on the flask and boil the solution gently on a steam bath for 15 min. Cool and dilute with 50 ml of water. Add approximately 0,2 g of sodium hydrogen carbonate (9.6.2.1), 3 drops of ferroin indicator solution (9.6.2.8) and then cerium(IV) sulfate solution (9.6.2.6), drop by drop, until the colour changes from red to yellow-green. Add approximately 0,2 g of sodium hydrogen carbonate and 4 g of potassium iodide (9.6.2.2), stopper the flask and swirl until the potassium iodide is completely dissolved. Place the flask in the dark for 15 min. Titrate with the sodium thiosulfate solution (9.6.2.7) until the colour changes from red-violet to pale yellow. Then add 3 to 4 ml of starch solution (9.6.2.9) and continue to titrate drop by drop, with shaking, until colourless.

9.6.4 Expression of results

The iron content, w_{Fe}, expressed as a percentage mass fraction, is given by Formula (9):

$$w_{Fe} = \frac{V_{11} \times T_2 \times 0{,}055\,85}{m_7} \times 100$$

$$= \frac{V_{11} \times T_2}{m_7} \times 5{,}585 \quad (9)$$

where

V_{11} is the volume, in millilitres, of sodium thiosulfate solution (9.6.2.7) required;

T_2 is the exact concentration of the sodium thiosulfate solution (9.6.2.7), in moles of $Na_2S_2O_3$ per litre;

m_7 is the mass, in grams, of the test portion.

9.7 Zirconium (EDTA titrimetric method)

9.7.1 Reagents

9.7.1.1 Acetic acid, glacial.

9.7.1.2 Acetone.

9.7.1.3 Sulfuric acid, $c(H_2SO_4)$ approximately 2 mol/l.

9.7.1.4 Ammonia, 10 % (mass fraction) solution.

9.7.1.5 Sodium acetate solution.

Dissolve 250 g of sodium acetate (CH_3COONa) in 750 ml of water.

9.7.1.6 EDTA, 0,100 mol/l standard volumetric solution (see 9.2.1.6).

9.7.1.7 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.2.1.7).

9.7.1.8 1,5-Diphenylthiocarbazone (dithizone), 0,1 % (mass fraction) solution in acetone.

9.7.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing approximately 120 mg of zirconium into a 250 ml conical flask. Add approximately 40 ml of sulfuric acid solution (9.7.1.3) and some boiling aids, heat to boiling and boil for 5 min. Cool, dilute with 60 ml of water and add 25 ml of EDTA solution (9.7.1.6) by means of a pipette.

Heat to boiling and boil for 3 min. Cool and add ammonia solution (9.7.1.4) until litmus paper gives a faintly alkaline reaction. Add successively 25 ml of sodium acetate solution (9.7.1.5), 50 ml of acetone (9.7.1.2) and 10 drops of dithizone solution (9.7.1.8). Add acetic acid (9.7.1.1) until the colour changes to blue-green (pH 4,1 to 4,4). Titrate with zinc sulfate solution (9.7.1.7) until the first change of the blue-green colour to red.

9.7.3 Expression of results

The zirconium content, w_{Zr}, expressed as a percentage mass fraction, is given by Formula (10):

$$w_{\mathrm{Zr}} = \frac{\left[(25 \times T_0) - (V_{12} \times T_1)\right] \times 0{,}091\,22}{m_8} \times 100$$

$$= \frac{(25 \times T_0) - (V_{12} \times T_1)}{m_8} \times 9{,}122 \qquad (10)$$

where

T_0 is the concentration of the EDTA solution (9.7.1.6), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.7.1.7), in moles of $ZnSO_4$ per litre;

V_{12} is the volume, in millilitres, of zinc sulfate solution (9.7.1.7) required;

m_8 is the mass, in grams, of the test portion.

9.8 Barium

9.8.1 General

For the determination of barium, two methods (method A and method B) are provided. If necessary, the method to be used should preferably be agreed between the interested parties, taking into account the limitation of method B with regard to the quantity of barium present.

9.8.2 Method A (gravimetric method)

9.8.2.1 Principle

The barium is precipitated as $BaSO_4$.

9.8.2.2 Reagents

9.8.2.2.1 Sulfuric acid, ρ approximately 1,84 g/cm^3.

9.8.2.2.2 Hydrogen peroxide, 30 % (mass fraction) solution.

9.8.2.3 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing 125 mg to 150 mg of barium into a 250 ml wide-necked conical flask. Add 10 ml of sulfuric acid (9.8.2.2.1) and, drop by drop, while stirring, 1 ml to 2 ml of hydrogen peroxide solution (9.8.2.2.2). Then add, drop by drop, while shaking, more hydrogen peroxide solution until the solution is only lightly coloured. Heat the solution to fuming. After cooling, add hydrogen peroxide solution as before and heat again. Repeat this procedure until the solution remains colourless after heating. After cooling, dilute slowly with 30 ml to 50 ml of water and boil for a short time.

Dilute the solution with approximately 150 ml of water, cover the flask and heat for 2 h to 3 h on a steam bath. Allow to stand overnight, and filter through a tared porcelain filter crucible. Wash with a small amount of water, dry for 15 min in an oven at (105 ± 2) °C and heat for 1 h in a furnace at 500 °C to 600 °C. Allow to cool in a desiccator and weigh to the nearest 1 mg.