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Driers for paints and varnishes

Siccatifs pour peintures et vernis

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Foreword

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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 4619 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

This second edition cancels and replaces the first edition (ISO 4619:1980), of which it constitutes an editorial revision.

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Driers for paints and varnishes

1 Scope

This International Standard specifies the requirements and the corresponding test methods for driers for paints, varnishes and related products. The requirements relate to driers in the solid or liquid form.

CAUTION — The procedures described in this International Standard 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 method may be injurious to health if adequate precautions are not taken. This International Standard refers only to its technical suitability and does not absolve the user from statutory obligations relating to health and safety.

Attention is particularly drawn to the health hazards of heavy metals which may be a constituent of driers (e.g. cobalt, lead, cerium, zirconium, vanadium; see clauses 3, 4 and 8).

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 150:1980, *Raw, refined and boiled linseed oil for paints and varnishes — Specifications and methods of test.*

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

ISO 1523:1983, *Paints and varnishes — Determination of flashpoint — Closed cup method.*

ISO 2431:1993, *Paints and varnishes — Determination of flow time by use of flow cups.*

ISO 2592:1973, *Petroleum products — Determination of flash and fire points — Cleveland open cup method.*

ISO 2811-1:1997, *Paints and varnishes — Determination of density — Part 1: Pyknometer method.*

ISO 3219:1993, *Plastics — Polymers/resins in the liquid state or as emulsions or dispersions — Determination of viscosity using a rotational viscometer with defined shear rate.*

ISO 3251:1993, *Paints and varnishes — Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes.*

ISO 3696:1987, *Water for analytical laboratory use — Specifications and test methods.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

3 Definition

For the purposes of this International Standard, the following definition applies.

3.1 drier: A 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 may 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.

NOTE — Emulsifiable driers are also available, but no requirements for this type are given in this International Standard.

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

4.3 Metals used

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

NOTE — In this International Standard, 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 comply with the requirement given in table 1.

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 — If desired, the type and content of the acids may 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 described in ISO 842.

Table 1 — Requirements and test methods

| Characteristic | | Requirement | Test method | |
|---|--------------------------------|---|---|---------------|
| | | | Solid driers | Liquid driers |
| Appearance | | Clear and uniform; no suspended matter or sediment | Subclause 7.1 | Subclause 8.1 |
| Consistency, if required | | | To be agreed between the interested parties | — |
| Colour | | As agreed between the interested parties | Subclause 7.2 | Subclause 8.2 |
| Solubility (miscibility) in solvent, raw linseed oil and other drying media | | No separation or deposit | Subclause 7.3 | Subclause 8.3 |
| Stability of solution | | Clear solution; no clouding gelation or sedimentation | Subclause 7.4 | Subclause 8.4 |
| Suspended solid matter | of liquid driers [% (m/m)] | max. 0,1 | Subclause 7.5 | Subclause 7.5 |
| | of solid driers | As agreed between the interested parties | | |
| Viscosity, only for liquid driers | | | | Subclause 8.5 |
| Volatile matter at 105 °C | | | Subclause 7.6 | Subclause 7.6 |
| Flashpoint | | | ISO 2592 | ISO 1523 |
| Density | | | To be agreed between the interested parties | ISO 2811-1 |
| Acidity or basicity | | | Subclause 7.7 | Subclause 7.7 |
| Drying characteristics | | | To be agreed between the interested parties | |
| Metal content (range) | up to 10 % (m/m) | ± 0,2 % ¹⁾ | Clause 9 or 10 | |
| | above 10 % (m/m) to 20 % (m/m) | ± 0,3 % ¹⁾ | | |
| | above 20 % (m/m) to 30 % (m/m) | ± 0,4 % ¹⁾ | | |
| | above 30 % (m/m) | ± 0,5 % ¹⁾ | | |

1) Tolerance (absolute value) on the metal content declared or agreed.

1) Tolerance (absolute value) on the metal content declared or agreed.

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 three 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, as a percentage by mass, using the formula

$$\frac{m_1}{m_0} \times 100$$

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 according to ISO 3251, taking a flat-bottomed glass of aluminium dish and a test portion of $(1 \pm 0,02)$ 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 or basicity

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, lead 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 % (*m/m*) solution.

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

7.7.2.6 Phenolphthalein, 1 % (*m/m*) solution in 96 % (*V/V*) ethanol.

7.7.3 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

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

7.7.4 Preparation of the ion-exchange column

Fill the ion-exchange column (7.7.3) 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/s (= 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 the propan-2-ol (7.7.2.2) and finally displace the propan-2-ol with 50 ml of a mixture (1 + 1) of the propan-2-ol and the toluene (7.7.2.3).

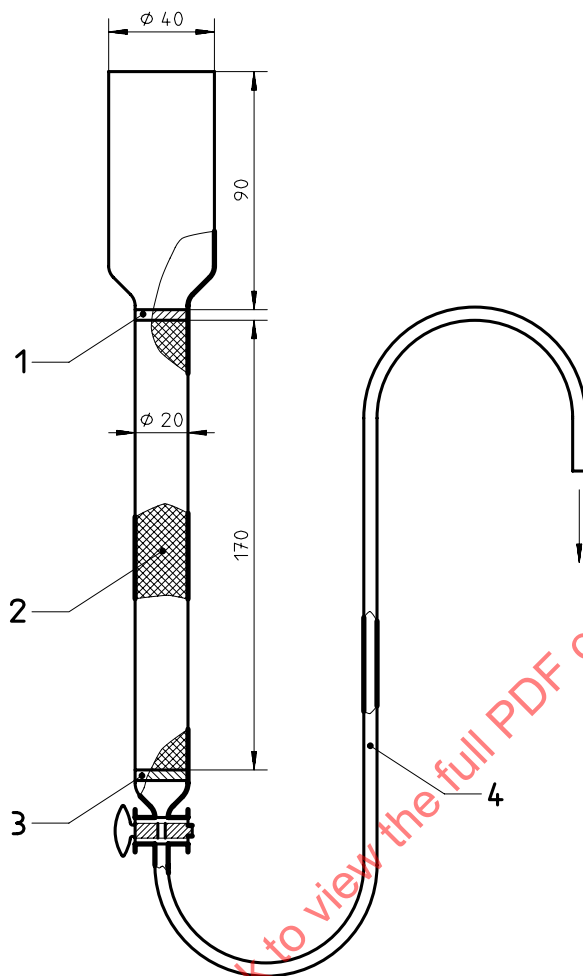
Do not use this column for more than about 50 milliequivalents of total metal.

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 it in 50 ml of the toluene (7.7.2.3). Dilute to the mark with the 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 the propan-2-ol and the 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.

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

Dimensions in millimetres

**Key**

- 1 Layer of glass wool
- 2 Ion-exchange resin
- 3 Sintered-glass disc
- 4 Capillary tubing Ø 2

Figure 1 — Example of a suitable ion-exchange column (see 7.7.3.1)**7.7.6 Expression of results**

The acidity or basicity, expressed in milligrams of potassium hydroxide (KOH) per gram, is given by the formula

$$56,1 \left(\frac{4 \times V \times T}{m} - \frac{10 \times c \times n}{A} \right)$$

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;
- c is the metal content, as a percentage by mass, 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 $\frac{c \times n}{A}$ 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

Prepare a mixture as follows:

| | |
|---|--------------------|
| Raw linseed oil, complying with ISO 150 (see the note): | 16 parts by volume |
| Mineral solvents. e.g. white spirit with an aromatic content of approximately 25 % (V/V) (see below): | 4 parts by volume |
| The drier under test (at standard strength) (see below): | 1 part by volume |

NOTE — 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 % (m/m)] be used instead of linseed oil.

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

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 % (m/m), as

| | | | |
|----|----|------|---------------------------|
| 6 | Co | 6 | Ce (or other rare earths) |
| 6 | Mn | 6 | Fe |
| 24 | Pb | 6 | Zr |
| 8 | Zn | 12,5 | Ba |
| 4 | Ca | | |

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:

- 0 °C;
- ambient temperature;
- 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

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

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.

9.1 Cobalt (EDTA titrimetric method)

9.1.1 Reagents

9.1.1.1 Hydroxylammonium chloride (OHNH_3Cl).

9.1.1.2 Propan-2-ol.

9.1.1.3 Ethanol, 96 % (V/V) solution.

9.1.1.4 Hydrochloric acid, $c(\text{HCl}) \approx 1 \text{ mol/l}$.

9.1.1.5 Hexamethylenetetramine, 40 % (m/m) aqueous solution.

9.1.1.6 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.

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

a) Preparation

Dissolve 14,38 g of zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) 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 (9.1.1.8) and 5 or 6 drops of Mordant black solution (9.1.1.9). Titrate with EDTA solution (9.1.1.6) 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 the equation

$$T_1 = \frac{V_1 \times T_0}{20}$$

where

V_1 is the volume, in millilitres, of EDTA solution (9.1.1.6) required for the titration;

T_0 is the concentration of the EDTA solution (9.1.1.6), in moles of EDTA per litre.

9.1.1.8 Buffer solution, pH 10.

Add 54 g of ammonium chloride and 350 g of ammonia solution (ρ approximately 0,91 g/ml) 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.

9.1.1.9 Mordant black 11²⁾, indicator solution.

Dissolve 0,5 g of Mordant black and 2,25 g of hydroxylammonium chloride (9.1.1.1) in 100 ml of ethanol (9.1.1.3).

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

9.1.2 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 (9.1.1.4) and heat to boiling.

Dilute with 100 ml of propan-2-ol (9.1.1.2), add 15 ml of hexamethylenetetramine solution (9.1.1.5) and 0,050 g of xylenol orange/potassium nitrate mixture (9.1.1.10). Titrate with EDTA solution (9.1.1.6) until the violet colour just changes to yellow.

If desired, back-titrate with zinc sulfate solution (9.1.1.7) until the first change of the yellow colour to red.

9.1.3 Expression of results

The cobalt content, expressed as a percentage by mass of Co, is given by the formula

$$\frac{[(V_2 \times T_0) - (V_3 \times T_1)] \times 0,058\,94}{m_2} \times 100$$

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

where

V_2 is the volume, in millilitres, of EDTA solution (9.1.1.6) required;

V_3 is the volume, in millilitres, of zinc sulfate solution (9.1.1.7) required (if used);

T_0 is the concentration of the EDTA solution (9.1.1.6), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.1.1.7), in moles of ZnSO_4 per litre;

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

9.2 Manganese (EDTA titrimetric method)

9.2.1 Reagents

9.2.1.1 Ascorbic acid or hydroxylammonium chloride (OHNH_3Cl).

9.2.1.2 Toluene.

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", etc. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

9.2.1.3 Propan-2-ol.**9.2.1.4 EDTA**, 0,100 mol/l standard volumetric solution (see 9.1.1.6).**9.2.1.5 Zinc sulfate**, approximately 0,05 mol/l standard volumetric solution (see 9.1.1.7).**9.2.1.6 Buffer solution**, pH 10 (see 9.1.1.8).**9.2.1.7 Mordant black 11**, indicator solution (see 9.1.1.9).**9.2.2 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 (9.2.1.2) and dilute with 50 ml of propan-2-ol (9.2.1.3). Add approximately 0,100 g of ascorbic acid or hydroxylammonium chloride (9.2.1.1). Add successively 10 ml of buffer solution (9.2.1.6) and 5 or 6 drops of Mordant black 11 solution (9.2.1.7). Titrate with EDTA solution (9.2.1.4) until the colour just changes from red to blue.

If desired, back titrate with zinc sulfate solution (9.2.1.5) until the first change of the blue colour to red.

9.2.3 Expression of results

The manganese content, expressed as a percentage by mass of Mn, is given by the formula

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

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

where

V_4 is the volume, in millilitres, of EDTA solution (9.2.1.4) required;

V_5 is the volume, in millilitres, of zinc sulfate solution (9.2.1.5) required (if used);

T_0 is the concentration of the EDTA solution (9.2.1.4), in moles of EDTA per litre;

T_1 is the concentration of the zinc sulfate solution (9.2.1.5), in moles of ZnSO_4 per litre;

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

9.3 Lead (EDTA titrimetric method)**9.3.1 Reagents****9.3.1.1 Toluene.****9.3.1.2 Propan-2-ol.****9.3.1.3 Acetic acid**, approximately 4 mol/l solution.**9.3.1.4 EDTA**, 0,100 mol/l standard volumetric solution (see 9.1.1.6).**9.3.1.5 Zinc sulfate**, approximately 0,05 mol/l standard volumetric solution (see 9.1.1.7).

9.3.1.6 Buffer solution, pH 10 (see 9.1.1.8).

9.3.1.7 Mordant black 11, indicator solution (see 9.1.1.9).

9.3.2 Procedure

Weigh, to the nearest 1 mg, a test portion of the drier containing 300 mg to 350 mg of lead into a 250 ml conical flask. Dissolve the test portion in 10 ml of toluene (9.3.1.1) and dilute with 50 ml of propan-2-ol (9.3.1.2). Add 5 ml of acetic acid solution (9.3.1.3) and 25 ml of EDTA solution (9.3.1.4) by means of a pipette. Add successively 10 ml of buffer solution (9.3.1.6) and 5 or 6 drops of Mordant black 11 solution (9.3.1.7). 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 lead content, expressed as a percentage by mass of Pb, is given by the formula

$$\frac{[(25 \times T_0) - (V_6 \times T_1)] \times 0,2072}{m_4} \times 100$$

$$= \frac{(25 \times T_0) - (V_6 \times T_1)}{m_4} \times 20,72$$

where

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;

V_6 is the volume, in millilitres, of zinc sulfate solution (9.3.1.5) required;

m_4 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 9.1.1.6).

9.4.1.4 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.1.1.7).

9.4.1.5 Buffer solution, pH 10 (see 9.1.1.8).

9.4.1.6 Mordant black 11, indicator solution (see 9.1.1.9).

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 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, expressed as a percentage by mass of Zn, is given by the formula

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

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

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, $c(\text{HCl}) \approx 4 \text{ mol/l}$.

9.5.1.4 EDTA, 0,100 mol/l standard volumetric solution (see 9.1.1.6).

9.5.1.5 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.1.1.7).

9.5.1.6 Buffer solution, pH 10 (see 9.1.1.8).

9.5.1.7 Mordant black 11, indicator solution (see 9.1.1.9).

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 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, expressed as a percentage by mass of Ca, is given by the formula

$$\frac{[(V_9 \times T_0) - (V_{10} \times T_1)] \times 0,040\,8}{m_6} \times 100$$

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

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;

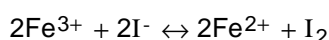
m_6 is the mass, in grams, of the test portion.

9.6 Iron (iodometric method)

NOTE — 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:



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 % (V/V) solution.

9.6.2.5 Sulfuric acid, $c(H_2SO_4) \approx 2$ 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, expressed as a percentage by mass of Fe, is given by the formula

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

$$= \frac{V_{11} \times T_2}{m_7} \times 5,585$$

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 $\text{Na}_2\text{S}_2\text{O}_3$ 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, $c(\text{H}_2\text{SO}_4) \approx 2\text{ mol/l}$.

9.7.1.4 Ammonia, 10 % (m/m) 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 9.1.1.6).

9.7.1.7 Zinc sulfate, approximately 0,05 mol/l standard volumetric solution (see 9.1.1.7).

9.7.1.8 1,5-Diphenylthiocarbazone (dithizone), 0,1 % (m/m) 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.