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Iron oxide pigments — Specifications and methods of test

Pigments à base d'oxydes de fer — Spécifications et méthodes d'essai

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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.

ISO 1248 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 2, *Pigments and extenders*.

This second edition cancels and replaces the first edition (ISO 1248:1974), which has been technically revised.

Iron oxide pigments — Specifications and methods of test

1 Scope

This International Standard specifies the requirements and the corresponding methods of test for all manufactured and natural iron oxide pigments, in dry form, suitable for general use. These pigments are identified by Colour Index Nos.[1] red 101 and 102, yellow 42 and 43, brown 6 and 7 and black 11, and includes “rapid-dispersion pigments”.

This International Standard does not cover micaceous iron oxide pigments (see Note 1), transparent iron oxide pigments, granular grey iron oxide (see Note 2) or magnetic iron oxide pigments other than those of Colour Index Pigment black 11.

NOTE 1 The requirements and the corresponding methods of test for micaceous iron oxide pigments are specified in ISO 10601.

NOTE 2 Granular grey iron oxides are too abrasive for general use.

2 Normative references

The following referenced documents are indispensable for the application 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 385–1, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 648, *Laboratory glassware — One-mark pipettes*

ISO 787-1, *General methods of test for pigments and extenders — Part 1: Comparison of colour of pigments*

ISO 787-2, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C*

ISO 787-3, *General methods of test for pigments and extenders — Part 3: Determination of matter soluble in water — Hot extraction method*

ISO 787-4, *General methods of test for pigments and extenders — Part 4: Determination of acidity or alkalinity of the aqueous extract*

ISO 787-5, *General methods of test for pigments and extenders — Part 5: Determination of oil absorption value*

ISO 787-7, *General methods of test for pigments and extenders — Part 7: Determination of residue on sieve — Water method — Manual procedure*

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[1] The Colour Index is published by The Society of Dyers and Colourists, PO Box 244, Perkin House, 82 Grattan Road, Bradford, West Yorkshire BD1 2JB, United Kingdom; and the American Association of Textile Chemists and Colorists, National Headquarters, Box 12215, Research Triangle Park, N.C. 27709, USA.

ISO 787-9, *General methods of test for pigments and extenders — Part 9: Determination of pH value of an aqueous suspension*

ISO 787-13, *General methods of test for pigments and extenders — Part 13: Determination of water-soluble sulfates, chlorides and nitrates*

ISO 787-16, *General methods of test for pigments and extenders — Part 16: Determination of relative tinting strength (or equivalent colouring value) and colour on reduction of coloured pigments — Visual comparison method*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

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

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

3 Description

The iron oxide pigments covered by this International Standard consist mainly of iron oxides and hydrated iron oxides. Their colours are usually red, yellow, brown or black.

4 Classification

4.1 General

In this International Standard, iron oxide pigments are classified as follows:

- by **groups** depending on their colour;
- by **categories** depending on their iron content, expressed as iron(III) oxide;
- by **types** depending on their content of water-soluble matter and their total content of water-soluble chlorides and sulfates, expressed as the ions Cl^- and SO_4^{2-};
- by **grades** depending on their residue on sieve;
- by **classes** depending on their origin.

4.2 Criteria for classification

4.2.1 Groups

Depending on their colour, iron oxide pigments are divided into four groups:

- reds;
- yellows;
- browns;
- blacks.

4.2.2 Categories

Depending on their minimum iron content, expressed as iron(III) oxide, iron oxide pigments are divided into the categories shown in Table 1.

Table 1 — Categories of iron oxide pigments

Group	Category	Minimum iron content, expressed as Fe_2O_3 % (by mass)	Colour Index No.
Red	A	95	Pigment red 101 77491
	B C D	70 50 10	Pigment red 102 77491
Yellow	A	83	Pigment yellow 42 77492
	B C D	70 50 10	Pigment yellow 43 77492
Brown	A	87	Pigment brown 6 77491, 77492 or 77499
	B C	70 30	Pigment brown 7 77491, 77492 and/or 77499
Black	A B	95 70	Pigment black 11 77499

4.2.3 Types

Depending on their content of water-soluble matter and their total content of water-soluble chlorides and sulfates, iron oxide pigments are divided into the types shown in Table 2.

Table 2 — Types of iron oxide pigments

Characteristic	Type I[a]	Type II		Type III	Method of test
	Red and brown only	Red and brown only	Yellow and black only	All pigments	
Matter soluble in water (determined after drying at 105 °C), % (by mass)	$\leqslant 0{,}3$	$> 0{,}3$ and $\leqslant 1$	$\leqslant 1$	> 1 and $\leqslant 5$	ISO 787-3
Sum of water-soluble chlorides and sulfates, expressed as the ions Cl^- and SO_4^{2-}, % (by mass)	$\leqslant 0{,}1$				ISO 787-13

[a] Type I pigments are used in making anticorrosive paints.

4.2.4 Grades

Depending on their residue on sieve, iron oxide pigments are divided into the grades shown in Table 3.

Table 3 — Grades of iron oxide pigments

Characteristic	Grade 1	Grade 2	Grade 3	Method of test
	Red, yellow, brown and black			
Residue on sieve (45 µm), % (by mass)	$\leqslant 0{,}01$	$> 0{,}01$ and $\leqslant 0{,}1$	$> 0{,}1$ and $\leqslant 1$	ISO 787-7

4.2.5 Classes

Depending on their origin, iron oxide pigments are divided into four classes:

- class a manufactured pigments without extenders;
- class b natural pigments without extenders;
- class c mixtures of natural and manufactured pigments without extenders;
- class d mixtures of pigments with extenders.

For classes a, b and c, the permitted maximum content of calcium (as CaO) is shown in Table 4.

5 Designation

The designation of an iron oxide pigment shall include the following.

a) An indication of the colour group to which it belongs, to which may be added a more precise indication of the actual colour (preferably by means of colorimetric data).

The following additional items may be included in this part of the designation:

- the common name in some countries, especially for natural pigments [ochre, umber, (terra di) Sienna, etc.];
- an indication of the treatment it has undergone (e.g. burnt, washed).

b) A reference to this International Standard, i.e. ISO 1248.

c) The category of the iron oxide pigment.

d) Its type.

e) Its grade.

f) Its class.

EXAMPLES

Red iron oxide ISO 1248-A-I-2-a

Yellow iron oxide (washed ochre) ISO 1248-D-II-3-b.

6 Required characteristics and associated tolerances

6.1 For iron oxide pigments complying with this International Standard, the essential requirements are specified in Table 4 and the conditional requirements are listed in Table 5. The conditional requirements shall be specified by agreement between the interested parties.

6.2 The agreed reference pigment referred to in Table 5 shall comply with the requirements of Table 4.

7 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

Table 4 — Essential requirements

Characteristic		Requirement depending on group and category													Method of test
		Red				Yellow				Brown			Black		
		A	B	C	D	A	B	C	D	A	B	C	A	B	
Total iron, expressed as iron(III) oxide (Fe_2O_3), determined on the pigment after drying at 105 °C, % (by mass) min.		95	70	50	10	83	70	50	10	87	70	30	95	70	See Clause 8
Matter volatile at 105 °C, % (by mass) max.		1	1,5	2,5	2,5	1	2,5	2,5	2,5	1	2,5	2,5	1	2,5	ISO 787-2
Matter soluble in water (hot extraction method), % (by mass)	Type I	$\leqslant 0{,}3$				—				$\leqslant 0{,}3$			—		ISO 787-3
	Type II	$> 0{,}3$ and $\leqslant 1$				$\leqslant 1$				$> 0{,}3$ and $\leqslant 1$			$\leqslant 1$		
	Type III	> 1 and $\leqslant 5$													
Water-soluble chlorides and sulfates, expressed as ions Cl^- and SO_4^{2-}, % (by mass)	Type 1	$\leqslant 0{,}1$				—				$\leqslant 0{,}1$			—		ISO 787-13
Residue on sieve (45 µm), % (by mass)	Grade 1	$\leqslant 0{,}01$													ISO 787-7
	Grade 2	$> 0{,}01$ and $\leqslant 0{,}1$													
	Grade 3	$> 0{,}1$ and $\leqslant 1$													
Acidity or alkalinity of aqueous extract solution, ml of 0,1 mol/l max.		20													ISO 787-4
Presence of lead chromate		Not detectable													See Clause 9
Total calcium, expressed as calcium oxide, determined on the pigment after drying at 105 °C, % (by mass) max.	Class a	0,3													See Clause 10
	Classes b and c	5													
	Class d	See Table 5													
Presence of organic colouring matter		Not detectable													See Clause 11

Table 5 — Conditional requirements for all groups and categories

Characteristic		Requirement	Method of test
pH value of the aqueous suspension		Shall not differ by more than 1 pH scale unit from that of the agreed reference pigment (see 6.2)	ISO 787-9
Oil absorption value		Shall not differ by more than 15 % from that of the agreed reference pigment (see 6.2)	ISO 787-5
Total calcium expressed as calcium oxide, % (by mass) max.	Class a	See Table 4	See Clause 10
	Classes b and c		
	Class d	To be agreed between the interested parties	
Colour		Equal to that of the agreed reference pigment (see 6.2) within a tolerance agreed between the interested parties	ISO 787-1
Relative tinting strength			ISO 787-16

8 Determination of total iron, expressed as iron(III) oxide (Fe_2O_3)

For the determination of the total iron content, two methods are provided. Method A (8.1) shall be used as the reference method in cases of dispute.

It is recommended that mercury be removed from the waste solutions before discharge to effluent drains. A suggested procedure is given in Annex A.

8.1 Method A

8.1.1 Principle

A test portion of the dried sample is dissolved in hydrochloric acid. The iron(III) is then reduced to iron(II) with tin(II) chloride solution, and the excess reducing agent is oxidized with mercury(II) chloride solution, followed by titration of the iron(II) with potassium dichromate solution, using sodium diphenylamine sulfonate as indicator.

8.1.2 Reagents

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

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

8.1.2.1 **Hydrochloric acid**, concentrated, approximately 37 % (by mass), $\rho \approx 1,19$ g/ml.

8.1.2.2 **Hydrochloric acid**, diluted 1 + 50.

Add 1 part by volume of concentrated hydrochloric acid (8.1.2.1) to 50 parts by volume of water.

8.1.2.3 **Hydrofluoric acid**, concentrated, approximately 40 % (by mass), $\rho \approx 1,13$ g/ml.

8.1.2.4 **Sulfuric acid**, diluted 1 + 1.

Add carefully 1 part by volume of concentrated sulfuric acid [approximately 96 % (by mass), $\rho \approx 1,84$ g/ml] to 1 part by volume of water.

8.1.2.5 Mixture of sulfuric and ortho-phosphoric acids

Carefully mix 310 ml of concentrated sulfuric acid [approximately 96 % (by mass), $\rho \approx 1,84$ g/ml] with 250 ml of concentrated orthophosphoric acid (H_3PO_4) [approximately 85 % (by mass), $\rho \approx 1,70$ g/ml]. Add the resultant mixture slowly to about 400 ml of water and then dilute with water to 1 litre.

8.1.2.6 Mercury(II) chloride, saturated solution (60 g/l to 100 g/l).

8.1.2.7 Tin(II) chloride, 100 g/l solution.

Dissolve 50 g of $SnCl_2 \cdot 2H_2O$ in 300 ml of concentrated hydrochloric acid (8.1.2.1) and dilute with water to 500 ml.

Keep the solution clear by storing it in an hermetically closed flask containing a small metallic tin.

8.1.2.8 Potassium dichromate, standard volumetric solution, $c(1/6\ K_2Cr_2O_7) = 0,1$ mol/l.

8.1.2.8.1 Preparation

Dissolve 4,903 g of $K_2Cr_2O_7$, previously dried at 150 °C for 60 min, in water and dilute to the mark in a 1 000 ml one-mark volumetric flask.

8.1.2.8.2 Standardization

Standardize the solution by using a standard Fe_2O_3 sample and the determination described in 8.1.4.

8.1.2.9 Sodium diphenylamine sulfonate indicator

Dissolve 0,2 g of sodium diphenylamine sulfonate in 100 ml of water.

8.1.2.10 Potassium pyrosulfate, $K_2S_2O_7$ (fine powder).

8.1.3 Apparatus

Use ordinary laboratory apparatus and burettes, pipettes and one-mark volumetric flasks complying with the requirements of ISO 385-1, ISO 648 or ISO 1042, respectively.

8.1.4 Procedure

8.1.4.1 Preliminary treatment of the test portion

8.4.1.1.1 Carry out the determination in duplicate.

8.1.4.1.2 Take a suitable quantity of the sample (see Clause 7) and dry it at 105 °C for 1 h. Weigh, to the nearest 0,1 mg, a test portion of the dried sample containing approximately 0,3 g of iron (see Table 1), i.e. 0,3 g to 1,0 g of the sample depending on the expected iron content.

8.1.4.1.3 If the sample is known, or suspected, to contain carbon or organic matter (see Note in 11.3), place the test portion in a 400 ml quartz beaker and ignite at 750 °C for 1 h, and allow to cool. Alternatively, place the test portion in a porcelain crucible, ignite at 750 °C for 1 h, allow to cool, and transfer to a 400 ml beaker.

8.1.4.1.4 Place the test portion in a 400 ml beaker and add 25 ml of hydrochloric acid (8.1.2.1). Cover the beaker with a watchglass and heat at 80 °C to 90 °C to dissolve the pigment. If an insoluble residue remains, add 50 ml of water, stir, and filter off the residue using a paper filter. Wash the filter with warm hydrochloric acid (8.1.2.2), until the yellow colour of iron(III) is no longer observed. Then wash once or twice with warm water. Place the filter and the residue in a platinum crucible, dry, char the paper and finally ignite at 750 °C to 800 °C. Allow the crucible to cool. Moisten the residue in the crucible with dilute sulfuric acid (8.1.2.4), add about 5 ml of hydrofluoric acid (8.1.2.3), and heat gently to remove silica and sulfuric acid.

8.1.4.1.5 Add to the cool crucible 2 g of potassium pyrosulfate (8.1.2.10), then heat gently at first and then more strongly, minimizing any tendency for the flux to creep, until a clear melt is obtained. Allow the melt to cool, place the platinum crucible in a 250 ml beaker, add about 50 ml of warm water and about 5 ml of hydrochloric acid (8.1.2.1), and heat gently to dissolve the melt. Remove and rinse the platinum crucible with water, collecting the rinsing fluids in the dissolved melt. Transfer the resulting solution to the original beaker.

8.1.4.2 Determination

Heat the combined filtrate until gently boiling. Avoid intense and prolonged boiling. Add, while stirring, the tin(II) chloride solution (8.1.2.7) drop by drop, until the last drop makes the solution colourless or free from yellow colour, then add one or two drops in excess. Dilute the solution to about 300 ml with cold water. Cool the solution in a water bath and then, whilst stirring vigorously, rapidly add 15 ml of mercury(II) chloride solution (8.1.2.6) to form a slight white precipitate which appears after 15 s to 20 s. One minute after adding the mercury(II) chloride, add 50 ml of sulfuric/phosphoric acid mixture (8.1.2.5) and 3 drops of sodium diphenylamine sulfonate indicator (8.1.2.9). Immediately begin to titrate slowly with potassium dichromate solution (8.1.2.8) to an endpoint when the dark green colour changes to violet. Record the volume of potassium dichromate solution used (V_1).

8.1.5 Expression of results

8.1.5.1 Calculation

Calculate the iron oxide content of the pigment, w, expressed as a percentage by mass, using the equation

$$w = \frac{V_1 \times 79{,}846 \times 0{,}1 \times 10^{-3} \times t}{m_1} \times 100\ \% \tag{1}$$

i.e. $$w = \frac{V_1 \times 0{,}798\,46 \times t}{m_1}\ \% \tag{2}$$

where

m_1 is the mass, in grams, of the test portion;

V_1 is the volume, in millilitres, of potassium dichromate solution (8.1.2.8) used in the determination;

$79{,}846 \times 0{,}1 \times 10^{-3}$ is the factor for the conversion of millilitres of potassium dichromate solution (8.1.2.8) to grams of Fe_2O_3;

t is the titre of the potassium dichromate solution, as determined in 8.1.2.8.2.

If the two determinations differ by more than 0,3 % (by mass), repeat the procedure.

Calculate the mean of two valid determinations and report the result to the nearest 0,1 % (by mass).

8.1.5.2 Precision

No precision data are currently available.

8.2 Method B

8.2.1 Principle

A test portion of the dried sample is dissolved in hydrochloric acid. The iron(III) is then reduced to iron(II) with titanium(III) chloride solution under an inert atmosphere, followed by titration of the iron(II) with potassium dichromate solution, using potentiometric indication of the endpoint.

8.2.2 Reagents

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

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

8.2.2.1 Hydrochloric acid, concentrated, approximately 37 % (by mass), $\rho \approx 1{,}19$ g/ml.

8.2.2.2 Hydrochloric acid, diluted 1 + 50.

Add 1 part by volume of concentrated hydrochloric acid (8.2.2.1) to 50 parts by volume of water.

8.2.2.3 Hydrofluoric acid, concentrated, approximately 40 % (by volume), $\rho \approx 1{,}13$ g/ml.

8.2.2.4 Sulfuric acid, diluted 1 + 1.

Add carefully 1 part by volume of concentrated sulfuric acid [approximately 96 % (by volume), $\rho \approx 1{,}84$ g/ml] to 1 part by volume of water.

8.2.2.5 Titanium(III) chloride ($TiCl_3$), 15 % (by mass) solution.

Dissolve the solid $TiCl_3$ in concentrated hydrochloric acid while blanketing the solution with nitrogen. Dilute to the desired concentration with distilled water which has been boiled under a nitrogen atmosphere to fully remove any oxygen; store under an inert atmosphere, e.g. nitrogen.

8.2.2.6 Potassium dichromate, standard volumetric solution, $c(1/6\ K_2Cr_2O_7) = 0{,}25$ mol/l.

8.2.2.6.1 Preparation

Dissolve 12,258 g of $K_2Cr_2O_7$, previously dried at 150 °C for 60 min, in water and dilute to the mark in a 1 000 ml one-mark volumetric flask.

8.2.2.6.2 Standardization

Standardize the solution by using a standard Fe_2O_3 sample and the determination described in 8.2.4.

8.2.2.7 Potassium pyrosulfate, $K_2S_2O_7$ (fine powder).

8.2.3 Apparatus

Use ordinary laboratory apparatus, and pipettes and one-mark volumetric flasks complying with the requirements of ISO 648 and ISO 1042, respectively, together with the following:

8.2.3.1 Automatic titrator

8.2.3.2 Platinum electrode

8.2.3.3 Silver/silver chloride electrode

8.2.4 Procedure

8.2.4.1 Preliminary treatment of the test portion

Carry out the determination in duplicate.

Take a suitable quantity of the sample (Clause 7) and dry it at 105 °C for 1 h. Weigh, to the nearest 0,1 mg, a test portion of the dried sample containing approximately 0,3 g of iron (see Table 1); i.e. 0,3 g to 1,0 g of the sample depending on the expected iron content.

Place the test portion in a 400 ml beaker (see 8.1.4.1.3) and add 25 ml of hydrochloric acid (8.2.2.1). Cover the beaker with a watchglass and heat at 80 °C to 90 °C to dissolve the pigment. If an insoluble residue remains, add 50 ml of water, stir, and filter off the residue using a paper filter. Wash the filter with warm hydrochloric acid (8.2.2.2), until the yellow colour of iron(**III**) is no longer observed. Then wash once or twice with warm water. Place the filter and the residue in a platinum crucible, dry, char the paper and finally ignite at 750 °C to 800 °C. Allow the crucible to cool. Moisten the residue in the crucible with dilute sulfuric acid (8.2.2.4), add about 5 ml of hydrofluoric acid (8.2.2.3), and heat gently to remove silica and sulfuric acid.

Add 2 g of potassium pyrosulfate (8.2.2.7) to the cool crucible. Heat gently at first and then more strongly, minimizing any tendency for the flux to creep, until a clear melt is obtained. Allow the melt to cool, place the platinum crucible in a 250 ml beaker, add about 50 ml of warm water and about 5 ml of hydrochloric acid (8.2.2.1), and heat gently to dissolve the melt. Remove and rinse the platinum crucible with water, collecting the rinsing fluids in the dissolved melt. Transfer the resulting solution to the original beaker.

8.2.4.2 Determination

Dilute the combined filtrate to about 300 ml with water, add 25 ml of hydrochloric acid (8.2.2.1) and heat to 80 °C to 90 °C. Add, while stirring and blanketing with an inert gas (e.g. nitrogen), titanium(**III**) chloride solution (8.2.2.5) drop by drop, until the last drop makes the solution colourless or free from yellow colour. Then add 1 to 2 drops in excess. The potential between the two electrodes is now below 300 mV.

Titrate the solution with potassium dichromate solution (8.2.2.6) in two stages. The volume of potassium dichromate solution required to reach a potential of 300 mV (V_2) corresponds to the oxidation of excess titanium(**III**). Continue the titration until there is a potential jump at 750 mV to 800 mV (total volume required is V_3).

8.2.5 Expression of results

8.2.5.1 Calculation

Calculate the iron oxide content, w, expressed as a percentage by mass, using the equation

$$w = \frac{(V_3 - V_2) \times 79{,}846 \times 0{,}25 \times 10^{-3} \times t}{m_2} \times 100\ \% \qquad (3)$$

$$\text{i.e. } w = \frac{(V_3 - V_2) \times 1{,}996\,2 \times t}{m_2}\ \% \qquad (4)$$

where

m_2	is the mass, in grams, of the test portion;
V_2	is the volume, in millilitres, of potassium dichromate solution (8.2.2.6) required to reach a potential of 300 mV;
V_3	is the total volume, in millilitres, of potassium dichromate solution (8.2.2.6) used in the determination;
$79{,}846 \times 0{,}25 \times 10^{-3}$	is the factor for the conversion of millilitres of potassium dichromate solution (8.2.2.6) to grams of Fe_2O_3;
t	is the titre of the potassium dichromate solution as determined in 8.2.2.6.2.

8.2.5.2 Precision

No precision data are currently available.

9 Test for presence of lead chromate

9.1 Reagents

During the test, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

9.1.1 Nitric acid, diluted 1 + 5.

Add 1 part by volume of concentrated nitric acid [approximately 70 % (by mass), $\rho \approx 1{,}42$ g/ml] to 5 parts by volume of water.

9.1.2 Potassium iodide, 100 g/l solution.

9.2 Procedure

Weigh approximately 1 g of the dried sample into a 250 ml beaker, add 100 ml of nitric acid (9.1.1) and stir vigorously. Filter, then add to the filtrate a few millilitres of potassium iodide solution (9.1.2).

The appearance of yellow crystals indicates the presence of lead.

10 Determination of total calcium

For the determination of total calcium, two methods are provided. The flame atomic absorption spectrometric (AAS) method (10.1) shall be used as the reference method in cases of dispute.

10.1 Flame atomic absorption spectrometric (AAS) method

10.1.1 Principle

A test portion of the dried sample is dissolved in hydrochloric acid. Any silica present is volatilized by hydrofluoric acid. The test solution is then aspirated into an acetylene/dinitrogen oxide flame, and the absorbency of the 422,7 nm spectral line emitted by a calcium hollow-cathode lamp or calcium discharge lamp is measured.

10.1.2 Reagents and materials

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

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

10.1.2.1 Hydrochloric acid, concentrated, approximately 37 % (by mass), $\rho \approx 1{,}19$ g/ml.

10.1.2.2 Hydrofluoric acid, concentrated, approximately 40 % (by mass), $\rho \approx 1{,}13$ g/ml.

10.1.2.3 Sulfuric acid, concentrated, approximately 96 % (by mass), $\rho \approx 1{,}84$ g/ml.

10.1.2.4 Caesium chloride, 76 g/l solution.

The caesium chloride used shall be of the highest purity available.

10.1.2.5 Calcium standard stock solution, containing 1 g/l of Ca.

Two preparations are acceptable:

a) transfer the contents of an ampoule of standard calcium solution containing exactly 1 g of Ca into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well; or

b) weigh, to the nearest 1 mg, 2,497 g of calcium carbonate, dissolve in approximately 5 ml of hydrochloric acid (10.1.2.1) in a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this standard stock solution contains 1 mg of Ca.

10.1.2.6 Calcium standard solution, containing 100 mg/l of Ca.

Prepare this solution on the day of use.

Pipette 100 ml of the standard stock solution (10.1.2.5) into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this standard solution contains 100 µg of Ca.

10.1.2.7 Acetylene, commercial grade, in a steel cylinder.

10.1.2.8 Dinitrogen oxide

10.1.3 Apparatus

Use ordinary laboratory apparatus, and burettes, pipettes and one-mark volumetric flasks complying with the requirements of ISO 385-1, ISO 648 and ISO 1042, respectively, together with the following:

10.1.3.1 Flame atomic absorption spectrometer, suitable for measurement at a wavelength of 422,7 nm and fitted with a burner suitable for use with acetylene and dinitrogen oxide.

10.1.3.2 Calcium hollow-cathode lamp or **calcium discharge lamp**.

10.1.4 Procedure

10.1.4.1 Preparation of the calibration graph

10.1.4.1.1 Preparation of the calibration solutions

Prepare these solutions on the day of use.

Into a series of seven 100 ml one-mark volumetric flasks, introduce from a burette the respective volumes of the standard calcium solution (10.1.2.6) shown in Table 6. Add 10 ml of caesium chloride solution (10.1.2.4) and 5 ml of hydrochloric acid (10.1.2.1) to each, dilute each to the mark with water and mix well.

Table 6 — Calibration solutions

Calibration solution No.	Volume of standard calcium solution (10.1.2.6) ml	Concentration of Ca in calibration solution µg/ml
0	0	0
1	0,2	0,2
2	1	1
3	2	2
4	4	4
5	8	8
6	10	10

10.1.4.1.2 Spectrometric measurements

Install the calcium spectral source (10.1.3.2) in the spectrometer (10.1.3.1) and optimize the conditions for the determination of calcium. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 422,7 nm in order to obtain the maximum absorbency.

Adjust the flow of acetylene (10.1.2.7) and dinitrogen oxide (10.1.2.8) to suit the characteristics of the burner, and ignite the flame. Set the scale expansion, if fitted, so that calibration solution No. 6 (see Table 6) gives almost full-scale deflection.

Aspirate into the flame each of the calibration solutions (see 10.1.4.1.1), starting with calibration solution No. 0, and repeating with calibration solution No. 5 after calibration solution No. 6 to verify that the instrument has remained stable. Aspirate water through the burner between each measurement, taking care to keep the rate of aspiration constant.

10.1.4.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Ca contained in 1 ml of the calibration solutions as abscise and the corresponding values of the absorbency, corrected for the value for calibration solution No. 0, as ordinates.

10.1.4.2 Preliminary treatment of the test portion

Carry out the determination in duplicate.

Take a suitable quantity of the sample (Clause 7) and dry it at 105 °C for 1 h. Weigh, to the nearest 1 mg, approximately 1 g of the dried sample into a 100 ml beaker and add 25 ml of hydrochloric acid (10.1.2.1). Cover the beaker with a watchglass and heat at 80 °C to 90 °C to dissolve the pigment. Evaporate the hydrochloric acid until the residue is almost dry. Add 50 ml of water and 5 ml of hydrochloric acid (10.1.2.1). Heat to dissolve the residue and filter the solution into a 100 ml one-mark volumetric flask. Make sure that any insoluble residue is completely transferred from the beaker to the filter. Then wash the filter once with warm water.

Ash the filter with the insoluble residue in a platinum crucible. Add 10 ml of hydrofluoric acid (10.1.2.2) and 0,5 ml of sulfuric acid (10.1.2.3) and carefully evaporate to dryness to volatilize any silica present. Dissolve the residue using the minimum amount of hydrochloric acid (10.1.2.1) and transfer the solution to the 100 ml one-mark volumetric flask. Add 10 ml of caesium chloride solution (10.1.2.4) and dilute to the mark with water.

10.1.4.3 Determination

Measure the absorbency of the test solution in the spectrometer (10.1.3.1) after having adjusted it as described in 10.1.4.1.2. If the absorbency is higher than that of the calibration solution with the highest calcium concentration, dilute the test solution appropriately (dilution factor F) with a known volume of water. Measure three times the absorbency of the test solution within the range of the calibration graph. Re-determine the absorbency of calibration solution No. 5 in order to verify that the response of the apparatus has not changed. Subtract from the three measurements the reading for calibration solution No. 0 and calculate the mean of the three corrected measurements. Read from the calibration graph the calcium concentration corresponding to the mean of the corrected measurements.

10.1.5 Expression of results

10.1.5.1 Calculation

Calculate the calcium oxide content of the pigment, $w_{(\mathrm{CaO})}$, expressed as a percentage by mass, using the equation

$$w_{(\mathrm{Cao})} = \frac{\rho_{(\mathrm{Ca})} \times 100 \times 1{,}399\,2 \times F}{m_3 \times 10^6} \times 100\ \% \tag{5}$$

$$\text{i.e. } w_{(\mathrm{CaO})} = \frac{\rho_{(\mathrm{Ca})} \times 1{,}399\,2 \times F}{m_3 \times 100}\ \% \tag{6}$$

where

$\rho_{(\mathrm{Ca})}$	is the calcium concentration of the test solution, in micrograms per millilitre, obtained from the calibration graph;
F	is the dilution factor referred to in 10.1.4.3;
m_3	is the mass, in grams, of the test portion;
1,399 2	is the factor for the conversion of grams of Ca to grams of CaO.

If the two determinations differ by more than the values given in Table 7, repeat the procedure.

Calculate the mean of two valid determinations and report the result to two significant figures.

Table 7 — Maximum acceptable difference between two determinations

Calcium content % (by mass)	Maximum difference % (by mass)
0,001 to 0,01	0,000 5
above 0,01 to 0,1	0,005
above 0,1 to 5	0,05

10.1.5.2 Precision

No precision data are currently available.

10.2 Titrimetric method

10.2.1 Principle

A test portion of the dried sample is dissolved in hydrochloric acid. The iron in the solution is extracted with methyl isobutyl ketone, and the calcium is precipated as calcium oxalate. The calcium oxalate is dissolved in sulfuric acid and the liberated oxalic acid is titrated with potassium permanganate solution.

10.2.2 Reagents

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

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

10.2.2.1 Hydrochloric acid, concentrated, approximately 37 % (by mass), $\rho \approx 1{,}19$ g/ml.

10.2.2.2 Hydrochloric acid, diluted 1 + 1.

Add 1 part by volume of concentrated hydrochloric acid (10.2.2.1) to 1 part by volume of water.

10.2.2.3 Hydrofluoric acid, concentrated, approximately 40 % (by mass), $\rho \approx 1{,}13$ g/ml.

10.2.2.4 Sulfuric acid, concentrated, approximately 96 % (by mass), $\rho \approx 1{,}84$ g/ml.

10.2.2.5 Sulfuric acid, diluted 1 + 4.

Add carefully 1 part by volume of concentrated sulfuric acid (10.2.2.4) to 4 parts by volume of water.

10.2.2.6 Acetic acid, concentrated, 99 % to 100 % (by mass).

10.2.2.7 Ammonia solution, concentrated, approximately 25 % (by mass), $\rho \approx 0{,}9$ g/ml, free from carbon dioxide.

10.2.2.8 Ammonium oxalate, saturated solution.

10.2.2.9 Ammonium oxalate, 1 g/l solution.

10.2.2.10 Potassium permanganate, standard volumetric solution, $c(1/5\ \mathrm{KMnO_4}) = 0{,}1$ mol/l.

Standardize the solution by using D-sodium oxalate, GR volumetric standard, and the titration described in 10.2.4.2.

10.2.2.11 Methyl red, 1 g/l solution in ethanol, at least 95 % (by volume).

10.2.2.12 Methyl isobutyl ketone.

10.2.3 Apparatus

Use ordinary laboratory apparatus, and burettes and one-mark volumetric flasks complying with the requirements of ISO 385-1 and ISO 1042, respectively.

10.2.4 Procedure

10.2.4.1 Preliminary treatment of the test portion

Carry out the determination in duplicate.

Take a suitable quantity of the sample (see Clause 7) and dry it at 105 °C for 1 h. Weigh, to the nearest 1 mg, a test portion of about 10 g of the dried sample into a porcelain dish.

Heat the porcelain dish with the test portion in an oven at 750 °C for 1 h. After cooling down, dissolve the test portion in 100 ml of concentrated hydrochloric acid (10.2.2.1) and evaporate to dryness. Heat the residue in an oven at 150 °C for 1 h, allow to cool down then dissolve in 50 ml of concentrated hydrochloric acid.

Dilute with 50 ml of water, filter and wash the filter with dilute hydrochloric acid (10.2.2.2).

Ash the filter with the insoluble residue in a platinum crucible. Add hydrofluoric acid (10.2.2.3) and sulfuric acid (10.2.2.4), and carefully evaporate to dryness to volatilize any silica present. Dissolve the residue in dilute hydrochloric acid (10.2.2.2) and add the solution to the filtrate obtained in the previous paragraph. Transfer the solution to a 250 ml separating funnel.

10.2.4.2 Determination

Add a further 60 ml of hydrochloric acid (10.2.2.2) to the separation funnel and extract the iron with 60 ml of methyl isobutyl ketone (10.2.2.12). If the solution does not become colourless, extract a second time. Draw off the aqueous phase, collecting it in a beaker, and neutralize with ammonia solution (10.2.2.7) in the presence of methyl red (10.2.2.11). Then acidify the solution with the acetic acid (10.2.2.6), adding a slight excess.

Boil the solution and add 50 ml of hot saturated ammonium oxalate solution (10.2.2.8). Continue boiling until the precipitate becomes granular. Allow to stand for approximately 1 h, filter and wash the filter paper with dilute ammonium oxalate solution (10.2.2.9) until chloride is no longer detectable in the washings. Complete the washing with the minimum of cold water to eliminate the ammonium oxalate.

Place the beaker under the filter funnel, pierce the tip of the filter paper with a glass rod and wash the precipitate down into the beaker with hot water. Pour approximately 30 ml of warm sulfuric acid (10.2.2.5) onto the paper to wash it, and dilute the solution in the beaker with water to approximately 250 ml. Titrate at about 75 °C with the potassium permanganate solution (10.2.2.10), ensuring that by the end of the titration the solution temperature is not below 60 °C. Record the volume of potassium permanganate solution used (V_4).

10.2.5 Expression of results

10.2.5.1 Calculation

Calculate the calcium oxide content of the pigment, $w_{(\text{CaO})}$, expressed as a percentage by mass, using the equation

$$w_{(\text{CaO})} = \frac{V_4 \times 28{,}04 \times 0{,}1 \times 10^{-3}}{m_4} \times 100\ \% \tag{7}$$

$$\text{i.e. } w_{(\text{CaO})} = \frac{0{,}280\ 4 \times V_4}{m_4}\ \% \tag{8}$$

where

m_4	is the mass, in grams, of the test portion;
V_4	is the volume, in millilitres, of potassium permanganate solution (10.2.2.10) used;
$28{,}04 \times 0{,}1 \times 10^{-3}$	is the factor for the conversion of millilitres of potassium permanganate solution to grams of CaO.

If the two determinations differ by more than 0,05 % (by mass), repeat the procedure.

Calculate the mean of two valid determinations and report the result to the nearest 0,1 % (by mass).

10.2.5.2 Precision

No precision data are currently available.

11 Test for organic colouring matter

11.1 Reagents

During the test, use only reagents of recognized analytical grade and only water of at least grade 3 purity as defined in ISO 3696.

WARNING —Use the reagents in accordance with the appropriate health and safety regulations.

11.1.1 Ethanol, at least 95 % (by volume).

11.1.2 Sodium hydroxide, ethanolic solution, c(NaOH) = 1 mol/l.

11.1.3 1,1,1-Trichloroethane.

11.2 Procedure

11.2.1 Test portion

Place about 2 g of the sample in each of two test tubes.

11.2.2 Determination

Boil one of the test portions with 25 ml of water, allow to settle and decant the supernatant liquid.

Boil the residue with 25 ml of ethanol (11.1.1) and decant as before.

Boil the second residue with 25 ml of sodium hydroxide solution (11.1.2), and again decant.

Boil the other test portion with 25 ml of 1,1,1-trichloroethane (11.1.3), allow to settle and decant the supernatant liquid.

Note the colours of the supernatant liquids.

11.3 Expression of results

Report if the above solutions are coloured or not. If one of the solutions is coloured, organic matter is present.

NOTE The absence of colour in these solutions indicates that there is most likely no or very little organic colouring matter in the pigment. The presence of organic colouring matter may also be detected by a characteristic smell when the pigment is calcined. See also 8.1.4.1.3.

12 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product tested;

b) a reference to this International Standard (ISO 1248);

c) the results of the tests, the method used where a choice is available, and whether or not the product complies with the relevant specification limits;

d) any deviation from the methods of test specified;

e) the date of the tests.

Annex A
(informative)

Decontamination of the waste solutions containing mercury

To avoid discharging to the environment the mercury contained in the waste solutions from the determination of iron, such solutions should be collected and processed for the removal of their mercury content.

A suitable treatment system may be constructed as follows (taken from Reference [2]).

Connect three 10-litre plastic bottles as illustrated in Figure A.1 (the expansion chamber incorporated in the connecting lines minimizes the risk of pressure increase in the case of a vigorous reaction). The first two bottles each contain 3 kg of aluminium or iron rods to induce mercury precipitation electrochemically.

Feed the solution discharged from the third bottle to a neutralization vessel before final discard. Remove accumulated mercury sludge from time to time and concentrate it by decantation before transfer to a recovery plant. Replace the aluminium or iron rods as necessary.

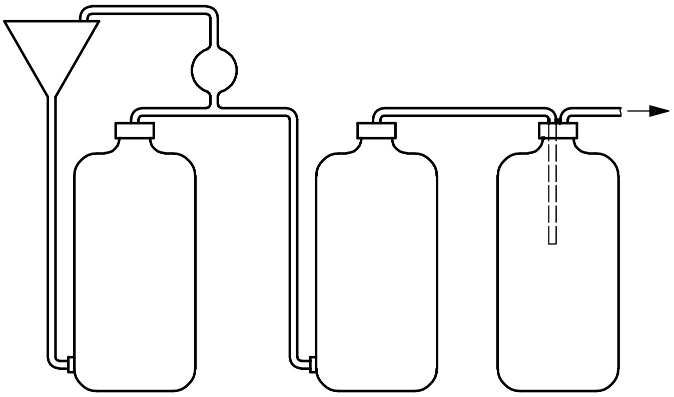

Figure A.1 — Apparatus for removal of mercury from waste solutions

Bibliography

[1] ISO 10601, *Micaceous iron oxide pigments for paints — Specifications and test methods*

[2] ANSMANN, W. *Arch. Eisenhüttenw.*, **53**(10), 1982, p. 390

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