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Zinc dust pigments for paints — Specifications and test methods

Pigments à base de poussière de zinc pour peintures — Spécifications et méthodes d'essai

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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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 document 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).

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This document was prepared by Technical Committee ISO/TC 256, *Pigments, dyestuffs and extenders,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 298, *Pigments and extenders,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This third edition cancels and replaces the second edition (ISO 3549:1995), which has been technically revised.

The main changes are as follows:

- the maximum residue on the 45 µm sieve has been changed from 5 % mass fraction to 0,5 % mass fraction;
- three types of zinc dust pigments (I, II and III) have been introduced with different requirements;
- inductively coupled plasma-optical emission spectroscopy (ICP-OES) has been added as an analytical technique used for elemental analysis;
- the nominal size of sieve aperture has been changed from 125 µm – 90 µm – 45 µm to 125 µm –75 µm – 45 µm;
- CAS Registry Numbers® have been added to the reagents;
- the normative references have been updated;
- a bibliography has been added.

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.

Zinc dust pigments for paints — Specifications and test methods

1 Scope

This document specifies the requirements and corresponding test methods for zinc dust pigments suitable for use in protective coatings.

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 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

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

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

3.1
zinc dust pigment
fine grey powder of essentially spheroidal particles, mainly consisting of metallic zinc

Note 1 to entry: Zinc dust pigments for paints can vary in their metallic zinc content, chemical purity, particle shape, particle size distribution, mean and maximum diameter, etc. These variations are all likely to have an influence on the zinc dust behaviour in paints with regard to parameters such as dispersibility, fineness of grind, reactivity, electrical conductivity and packing properties.

4 Required characteristics and tolerances

4.1 For zinc dust pigments conforming to this document, the essential requirements are specified in Table 1 and Table 2.

Table 1 — Composition of zinc dust pigment

Characteristic	Unit	Requirement			Test method
		Type I	Type II	Type III	
Total zinc content	% (mass fraction)	min. 98	min. 98	min. 99	See Clause 7
Metallic zinc content	% (mass fraction)	min. 94	min. 94	min. 97	See Clause 8
Lead (Pb) content	% (mass fraction)	max. 0,1	max. 0,01	max. 0,002	See Clause 9[a]
Cadmium (Cd) content	% (mass fraction)	max. 0,03	max. 0,01	max. 0,001	See Clause 9[a]
Iron (Fe) content	% (mass fraction)	max. 0,005	max. 0,005	max. 0,002	See Clause 9[a]
Arsenic (As) content	% (mass fraction)	max. 0,000 5	max. 0,000 5	max. 0,000 5	See Clause 10[a]
Chloride (Cl) content	% (mass fraction)	max. 0,005	max. 0,005	max. 0,005	See Clause 11
Matter insoluble in acid	% (mass fraction)	max. 0,05	max. 0,05	max. 0,05	See Clause 12

[a] Other suitable methods such as the induction coupled plasma (ICP-OES or ICP-MS) method may be agreed upon between the interested parties.

NOTE If the zinc oxide content is required, this can be calculated by multiplying the difference between the total zinc content and the metallic zinc content by 1,244 7.

Table 2 — Residue on sieve

Nominal size of sieve aperture µm	Residue on sieve % (mass fraction)	Test method
125	max. 0,01	See Clause 6
75	max. 0,1	
45	max. 0,5	

4.2 Requirements for other physical properties (surface area, particle size distribution, etc.) and the choice of reference pigment to which these properties refer shall be the subject of agreement between the interested parties. Particle size and/or particle size distribution data as D10(1), D50(2), shall be given with reference to the measurement method and test conditions.

4.3 The reference pigment shall also conform to the requirements given in Table 1 and Table 2.

4.4 Inductively coupled plasma–optical emission spectroscopy (ICP-OES) is an analytical technique used for elemental analysis. The ICP-OES instrument is used in atomic spectroscopy. During analysis, the sample is decomposed by intense heat into a cloud of hot gases containing free atoms and ions of the element(s) of interest. The high temperatures cause significant amounts of collisional excitation and ionization of the sample atoms. Once the atoms or ions are in their excited state, they can decay to lower states through thermal or radiative (emission) energy transitions. During ICP-OES analysis, the intensity of the light emitted at specific wavelengths is measured and used to determine the concentration of the element(s) of interest. In ICP-OES analysis the thermal excitation sources can populate a large number of different energy levels for several different elements at the same time. All of the excited atoms and ions can then emit their

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1) Industry term meaning the value of the particle diameter below which 10 % of the particles fall in the cumulative particle size distribution.

2) Industry term meaning the value of the particle diameter below which 50 % of the particles fall in the cumulative particle size distribution. It is also known as the median diameter.

characteristic radiation at the same time. This results in the flexibility to choose from several different emissions concurrently and allows detection of multiple elements concurrently.

Sample preparation for ICP-OES analysis is very similar to the sample preparation for atomic absorption (AA; see Clause 9 and Clause 10) with a variant. (0,500 0 ± 0,000 2) g of sample is dissolved in 100 ml 5 % (volume fraction) HNO_3 68 % (mass fraction). For very resistant samples, an additional 10 % (volume fraction) HCl 37 % (mass fraction) may be used in combination with microwave digestion. The 5 g/l solutions are further diluted (1/200) with 5 % (volume fraction) HNO_3 while adding 50 µg/l of Sc, Y, Rh and Lu as internal standards. ICP measurement and standard preparation can be derived from ISO 22036.

5 Sampling

Take a representative sample of the product to be tested, in accordance with ISO 15528.

WARNING — The sample shall not be dried before testing, and any portion of the sample not used shall not be returned to the sample container after having been manipulated.

6 Determination of residue on sieve

6.1 Principle

A suitable test portion of the sample is passed through an air-jet sieve apparatus, having sieves with nominal mesh apertures of 45 µm, 75 µm and 125 µm. The residue on each of these sieves is determined.

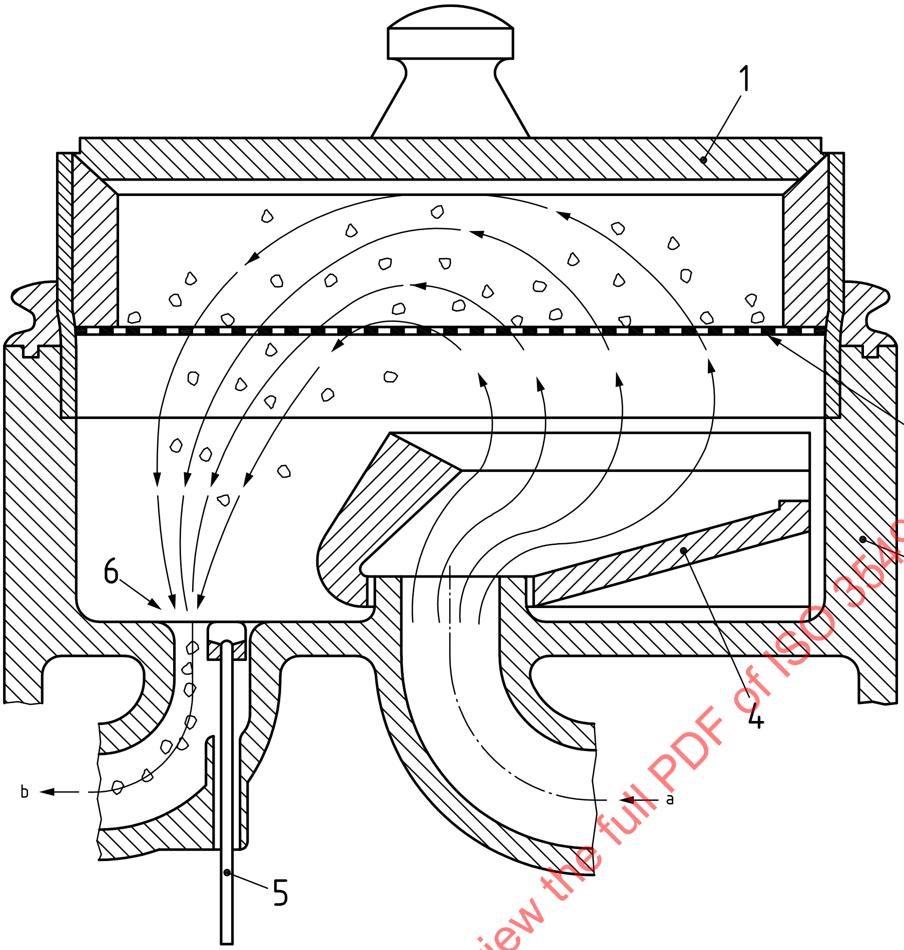
6.2 Apparatus

6.2.1 Sieves, circular, with a sieving area of diameter 200 mm and with nominal mesh apertures of 45 µm, 75 µm and 125 µm, conforming to ISO 565. A transparent lid shall be provided to cover the sieve during use.

6.2.2 Air-jet sieve apparatus (see Figure 1), consisting of a cylindrical casing which contains a sieve (see 6.2.1). The base of the casing has an outlet (to which an extractor fan is connected) and an air inlet to permit the injection of air.

The air inlet is connected to a jet rotating at 20 min^{-1} to 25 min^{-1} and consists of a slot-shaped nozzle located beneath and very close to the sieve (see Figure 1). When the jet rotates, it blows air continuously through the sieve, preventing the powder particles from settling. The air is extracted through the outlet, drawing the finer particles through the sieve. The flow of air is controlled by adjusting a slot at the outlet.

The vacuum obtained shall be 1 250 Pa or lower.



Key

1	transparent lid
2	sieve
3	casing
4	rotating jet
5	manometer
6	adjustable slot
a	Air inlet.
b	To extractor fan.

Figure 1 — Air-jet sieve apparatus

6.2.3 Timer (for example a stopwatch), recording to the nearest 1 s or better. It may be equipped with a switch for stopping the motor of the sieve apparatus (6.2.2).

6.2.4 Analytical balance, capable of weighing at least 50 g to the nearest 1 mg.

6.2.5 Mallet, of light construction, with a plastic head, suitable for tapping the apparatus to dislodge powder adhering to the lid and sieve.

6.2.6 Clean brush

6.2.7 Stainless-steel boat

6.3 Checking and cleaning the sieve

Check that the sieve is clean, undamaged and not blocked by material used in a previous determination. A magnifying glass of sufficient magnification is recommended to aid this inspection.

If cleaning of the sieve is necessary, an ultrasonic system is recommended for this purpose. It is also possible to clean the sieve by turning it upside down on a clean sheet of paper and tapping vigorously to eliminate any residual particles.

6.4 Procedure

Carry out the determination in duplicate.

6.4.1 Weigh, to the nearest 1 mg, a test portion of approximately 50 g (m_0).

6.4.2 Secure the 45 µm sieve (6.2.1) in position in the sieve apparatus (6.2.2) and transfer the test portion to the sieve.

6.4.3 Cover the sieve with the transparent lid, switch on the extractor fan and sieve apparatus (6.2.2) and tap the lid and the sieve lightly from time to time with the mallet (6.2.5) to distribute the material and dislodge adhering particles.

6.4.4 After 120 s, switch off the apparatus and remove the transparent lid and sieve. Recover the sieve residue by turning the sieve upside down on a clean sheet of paper and tapping vigorously to ensure that all particles are recovered.

6.4.5 Weigh the stainless-steel boat (6.2.7) to the nearest 1 mg (m_1). Transfer the sieve residue to it and reweigh to the nearest 1 mg (m_2).

6.4.6 Repeat the operations described in 6.4.1 to 6.4.5 with the 75 µm sieve and then with the 125 µm sieve on fresh 50 g portions of the sample.

6.5 Expression of results

Calculate the residue on each sieve, R, expressed as mass fraction in percent, using Formula (1):

$$R = \frac{(m_2 - m_1)}{m_0} \times 100 \qquad (1)$$

where

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

m_1 is the mass, in grams, of the steel boat;

m_2 is the mass, in grams, of the boat and the sieve residue.

If the two results (duplicates) for each sieve differ by more than one tenth of the maximum limit for that sieve in Table 2, repeat the procedure.

Calculate the mean of two valid results (replicates) and report the result to three decimal places for the 125 µm sieve, two decimal places for the 75 µm sieve and one decimal place for the 45 µm sieve.

7 Determination of total zinc content

7.1 Principle

The zinc is titrated against (ethylenedinitrilo)tetraacetic acid (EDTA) solution.

7.2 Reagents

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

7.2.1 Hydrochloric acid, CAS Registry Number®[3] 7647-01-0, concentrated, 37 % (mass fraction), $\rho \approx 1{,}19$ g/ml.

7.2.2 Hydrochloric acid, CAS RN 7647-01-0, diluted 1 + 4.

Dilute 200 ml of concentrated hydrochloric acid (7.2.1) to 1 l with water.

7.2.3 Sulfuric acid, CAS RN 7664-93-9, diluted 1 + 1.

Slowly add, while cooling, 1 part by volume of concentrated sulfuric acid [approximately 96 % (mass fraction), $\rho \approx 1{,}84$ g/ml] to 1 part by volume of water.

7.2.4 Nitric acid, CAS RN 7697-37-2, concentrated, approximately 68 % (mass fraction), $\rho \approx 1{,}42$ g/ml.

7.2.5 Ammonia solution, CAS RN 1336-21-6, approximately 25 % (mass fraction), $\rho \approx 0{,}81$ g/ml.

7.2.6 Buffer solution

Dissolve 200 g of hydroxylammonium chloride ($NH_2OH \cdot HCl$) (CAS RN 5470-11-1) in approximately 300 ml of water. Dissolve 28 g of sodium hydroxide (CAS RN 1310-73-2) in approximately 300 ml of water. Combine the two solutions, cool and dilute to 1 l with water.

7.2.7 (Ethylenedinitrilo)tetraacetic acid (EDTA), disodium salt dihydrate, CAS RN 6381-92-6, standard volumetric solution.

7.2.7.1 Preparation

Weigh, to the nearest 1 mg, about 20 g of disodium EDTA dihydrate, dissolve in water and make up to 1 l. Store in a polyethylene bottle.

7.2.7.2 Standardization

Weigh, to the nearest 1 mg, approximately 1,5 g of 99,99 % pure zinc metal (m_0) into a 250 ml beaker. Dissolve in 20 ml of hydrochloric acid (7.2.1) and add 1 ml or 2 ml of nitric acid (7.2.4). After complete dissolution, transfer quantitatively into a 500 ml volumetric flask, make up to the mark with water and mix thoroughly.

Pipette 50 ml of the zinc solution into a 500 ml conical flask. Add 200 ml of water and 3 drops of bromothymol blue indicator (7.2.9), followed by ammonia solution (7.2.5), drop by drop, until the colour changes to blue. Then add dilute hydrochloric acid (7.2.2) until the yellow colour returns. Finally add 20 ml of buffer solution (7.2.6) and 3 drops of xylenol orange indicator (7.2.8) and titrate with EDTA solution (7.2.7.1) until the red colour changes to pale yellow.

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[3] Chemical Abstracts Service (CAS) Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Calculate the zinc equivalent of the EDTA solution, $\rho(\mathrm{Zn})$, expressed in grams per millilitre (i.e. the mass, in grams, of zinc forming a complex with 1 ml of EDTA solution), using Formula (2):

$$\rho(\mathrm{Zn}) = \frac{m_0 \times 50}{500 \times V_0} = \frac{m_0}{10 \times V_0} \tag{2}$$

where

m_0 is the mass, in grams, of zinc metal used;

V_0 is the volume, in millilitres, of EDTA solution used for the titration.

Carry out the titration three times and calculate the mean value of the zinc equivalent $\rho(\mathrm{Zn})$, in grams per millilitre.

7.2.8 Xylenol orange, CAS RN 1202864-39-8, 1 g/l indicator solution of the sodium salt in water.

7.2.9 Bromothymol blue, CAS RN 76-59-5, 1 g/l indicator solution in 96 % (volume fraction) ethanol.

7.3 Procedure

7.3.1 Test portion

Weigh, to the nearest 1 mg, 1,5 g of the sample (m_1) into a 250 ml beaker.

7.3.2 Determination

Carry out the determination in duplicate.

Dissolve the test portion in 20 ml of concentrated hydrochloric acid (7.2.1) and add 1 ml or 2 ml of nitric acid (7.2.4) to ensure that any lead present is dissolved. Add 5 ml of sulfuric acid (7.2.3) and evaporate until dense white fumes appear. Cool, then add 100 ml of water, boil for a short time and allow to stand until the following day.

Filter the solution through a sintered-glass or silica filter crucible (P40 porosity); wash the beaker and the crucible, collecting the filtrate in a 500 ml one-mark volumetric flask. Make the solution up to the mark and mix thoroughly.

Pipette 50 ml of the solution into a 500 ml conical flask. Add 200 ml of water and 3 drops of bromothymol blue indicator (7.2.9), followed by ammonia solution (7.2.5), drop by drop, until the colour changes to blue. Then add dilute hydrochloric acid (7.2.2) until the yellow colour returns. Finally add 20 ml of buffer solution (7.2.6) and 3 drops of xylenol orange indicator (7.2.8) and titrate with EDTA solution (7.2.7) until the red colour changes to pale yellow.

7.4 Expression of results

Calculate the total zinc content, $w(\mathrm{Zn})_\mathrm{t}$, expressed as a percentage by mass, using Formula (3):

$$w(\mathrm{Zn})_\mathrm{t} = \frac{1\,000 \times V_1 \times \rho(\mathrm{Zn})}{m_1} \tag{3}$$

where

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

$\rho(\mathrm{Zn})$ is the zinc equivalent, in grams per millilitre, of the EDTA solution;

V_1 is the volume, in millilitres, of EDTA solution used.

If the two results (duplicates) differ by more than 0,5 % (mass fraction), repeat the procedure.

Calculate the mean of two valid results (replicates) and report the result to one decimal place.

8 Determination of metallic zinc content

8.1 Principle

Iron (III) sulfate solution and, as a catalyst, copper (II) sulfate solution are added to a test portion of the zinc dust pigment. The zinc is dissolved as zinc sulfate and the resulting iron (II) sulfate is titrated against potassium permanganate solution.

8.2 Reagents and materials

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

8.2.1 Nitrogen, CAS RN 7727-37-9, commercial grade, in a cylinder.

8.2.2 Orthophosphoric acid, CAS RN 7664-38-2, approximately 85 % (mass fraction), $\rho \approx 1{,}71$ g/ml.

8.2.3 Sulfuric acid, CAS RN 7664-93-9, diluted 1 + 19.

Slowly add, while cooling, 1 part by volume of concentrated sulfuric acid [approximately 96 % (mass fraction), $\rho \approx 1{,}84$ g/ml] to 19 parts by volume of water.

8.2.4 Copper (II) sulfate, solution.

Dissolve 200 g of copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) (CAS RN 7758-99-8) in 1 l of water.

8.2.5 Iron (III) sulfate, saturated solution.

Dissolve, as far as possible, 330 g of iron (III) sulfate [$Fe_2(SO_4)_3$] (CAS RN 7720-78-7) in 1 l of cold water. Heat until dissolution is complete. Allow to cool to room temperature, then filter.

8.2.6 Potassium permanganate, CAS RN 7722-64-7, standard volumetric solution, $c(KMnO_4) \approx 0{,}06$ mol/l.

8.2.6.1 Preparation

Weigh 20 g of potassium permanganate ($KMnO_4$) into a 3 l or 4 l flask and add 2 l of water. Boil for 1 h, allow to cool and allow to stand until the following day.

Decant through a filter of glass wool or a sintered-glass filter of pore size 0,5 µm into a 2 000 ml one-mark volumetric flask, make up to the mark with water and mix well. Transfer to a brown-glass bottle fitted with a glass stopper.

8.2.6.2 Standardization

Weigh, to the nearest 1 mg, 0,72 g of sodium oxalate (m_0) (CAS RN 62-76-0), which has been dried for 1 h at 105 °C, into a 500 ml conical flask. Dissolve in approximately 200 ml of dilute sulfuric acid (8.2.3).

Heat to boiling and titrate with the potassium permanganate solution (8.2.6.1) until a pink colour just appears (volume of potassium permanganate solution used: V_0).

Calculate the amount-of-substance concentration of the potassium permanganate solution, $c(\mathrm{KMnO_4})$, expressed in moles per litre, using Formula (4):

$$c(\mathrm{KMnO_4}) = \frac{2 \times m_0}{5 \times V_0 \times M_{\mathrm{ox}}} \times 1\ 000 \tag{4}$$

where

m_0 is the mass, in grams, of sodium oxalate used;

V_0 is the volume, in millilitres, of potassium permanganate solution used for the titration;

M_{ox} is the molar mass, in grams per mole, of sodium oxalate (M_{ox} = 134,00 g/mol).

Carry out the titration three times and calculate the mean value of the amount-of-substance concentration of the potassium permanganate solution, $c(\mathrm{KMnO_4})$, in moles per litre.

Carry out this standardization before using the solution.

8.3 Procedure

8.3.1 General

Carry out the determination in duplicate and as rapidly as possible. Ensure that the flask is kept stoppered as much as possible.

8.3.2 Test portion

Take a dry 750 ml conical flask and fill it with nitrogen (8.2.1). Stopper the flask carefully with a rubber bung. Weigh, to the nearest 0,1 mg, about 0,4 g of the sample (m_1) and quickly wash it into the flask with 4 ml or 5 ml of water from a water jet. Immediately replace the rubber bung. Prevent the formation of agglomerates as far as possible by shaking regularly.

8.3.3 Determination

Add to the flask 10 ml of copper (II) sulfate solution (8.2.4) and shake vigorously for about 1 min to prevent the formation of agglomerates. Then, using a pipette, wash down the neck of the flask to remove any metallic particles with 50 ml of iron (III) sulfate solution (8.2.5), which has previously been deoxygenated by passing a stream of nitrogen (8.2.1) through it for 10 min.

Allow to stand, shaking frequently, until dissolution is complete. This takes 15 min to 30 min.

When dissolution is complete, add 20 ml of orthophosphoric acid (8.2.2) and 200 ml of dilute sulfuric acid (8.2.3) and titrate immediately with potassium permanganate solution (8.2.6) until a faint pink colour is obtained (volume of potassium permanganate solution used: V_1).

Carry out a blank test, omitting the test portion (volume of potassium permanganate solution used: V_2).

8.4 Expression of results

Calculate the metallic zinc content, $w(\mathrm{Zn})_\mathrm{m}$, expressed as a percentage by mass, using Formula (5):

$$w(\mathrm{Zn})_\mathrm{m} = \frac{5(V_1 - V_2) \times \bar{c}(\mathrm{KMnO_4}) \times M(\mathrm{Zn}) \times 100}{2 m_1 \times 1\ 000} = 16{,}34 \times \frac{(V_1 - V_2) \times \bar{c}}{m_1} \tag{5}$$

where

$\bar{c}$ ($KMnO_4$)	is the mean amount-of-substance concentration, in moles per litre, of the potassium permanganate solution;
m_1	is the mass, in grams, of the test portion;
V_1	is the volume, in millilitres, of potassium permanganate solution used in the determination;
V_2	is the volume, in millilitres, of potassium permanganate solution used in the blank test;
M(Zn)	is the molar mass, in grams per mole, of zinc [M(Zn) = 65,37 g/mol].

If the two results (duplicates) differ by more than 0,5 % (mass fraction), repeat the procedure.

Calculate the mean of two valid results (replicates) and report the result to one decimal place.

9 Determination of lead, cadmium and iron content

9.1 Principle

A test solution is aspirated into an acetylene/air flame in an atomic absorption spectrometer and the absorption is measured at selected spectral emission lines of hollow-cathode lamps or discharge lamps.

9.2 Reagents and materials

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

9.2.1 Nitric acid, CAS RN 7697-37-2, concentrated, approximately 68 % (mass fraction), $\rho \approx 1{,}42$ g/ml.

9.2.2 Metallic lead, CAS RN 7439-92-1, 99,99 % (mass fraction) minimum purity.

9.2.3 Metallic cadmium, CAS RN 7440-43-9, 99,99 % (mass fraction) minimum purity.

9.2.4 Metallic iron, CAS RN 7439-89-6, 99,99 % (mass fraction) minimum purity.

9.2.5 Metallic zinc, CAS RN 7440-66-6, 99,999 9 % (mass fraction) minimum purity.

9.2.6 Lead, cadmium and iron, standard stock solution containing 1 g of each metal/l.

Weigh, to the nearest 0,1 mg, 1 g of cadmium (9.2.3) and 1 g of iron (9.2.4) into a 500 ml beaker. Dissolve the metals in approximately 20 ml of concentrated nitric acid (9.2.1), with heating, after covering with a watch glass. After complete dissolution, add approximately 40 ml of water. Weigh, to the nearest 0,1 mg, 1 g of lead (9.2.2) and introduce it into the beaker. Heat again for a few minutes and, after complete dissolution, heat to boiling and allow to boil gently for about 5 min. Allow to cool to room temperature and transfer quantitatively to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

1 ml of this standard stock solution contains 1 mg each of lead, cadmium and iron.

9.2.7 Lead, cadmium and iron, standard solution containing 50 mg of each metal/l.

By means of a pipette, transfer 25 ml of the solution obtained as described in 9.2.6 into a 500 ml one-mark volumetric flask, make up to the mark with water and mix well.

1 ml of this standard solution contains 50 µg each of lead, cadmium and iron.

9.2.8 **Lead, cadmium and iron,** calibration solutions.

These dilute solutions shall not be used after storage of more than one month.

9.2.8.1 For calibration in the range of 0,000 1 % to 0,01 %

Weigh, to the nearest 10 mg, 10 g of zinc (9.2.5) into each of five 300 ml beakers. By means of pipettes, add respectively 0 ml, 2 ml, 6 ml, 10 ml and 20 ml of the standard solution (9.2.7). Dissolve in approximately 50 ml of concentrated nitric acid (9.2.1) and cover the beakers with watch glasses. After complete dissolution, heat to boiling, then allow to cool to room temperature, and transfer quantitatively to five 100 ml one-mark volumetric flasks. Make up to the mark with water, mix well and transfer to polyethylene bottles, which are then hermetically closed for storage.

These five calibration solutions contain, respectively, 0 mg, 1 mg, 3 mg, 5 mg and 10 mg of lead, cadmium and iron per litre.

9.2.8.2 For calibration in the range of 0,01 % to 1 %

Pipette respectively 0 ml, 2 ml, 6 ml, 10 ml and 20 ml of the standard solution (9.2.7) into five 100 ml one-mark volumetric flasks. Add approximately 10 ml of concentrated nitric acid (9.2.1) to each. Make up to the mark with water, mix well and transfer to polyethylene bottles, which are then hermetically closed for storage.

These five calibration solutions contain, respectively, 0 mg, 1 mg, 3 mg, 5 mg and 10 mg of lead, cadmium and iron per litre.

9.2.9 **Acetylene,** CAS RN 74-86-2, commercial grade, in a cylinder.

9.3 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

9.3.1 **Flame atomic absorption spectrometer,** fitted with hollow-cathode lamps or an electrodeless discharge lamp for lead, cadmium and iron, and with a nebulizer-burner fed with acetylene and air.

9.3.2 **Polyethylene bottles,** 500 ml, with double closure.

9.4 Procedure

9.4.1 Test portion

For determination in the range of 0,000 1 % to 0,01 %: weigh, to the nearest 1 mg, 10 g of the sample.

For determination in the range of 0,01 % to 1 %: weigh, to the nearest 1 mg, 1 g of the sample.

9.4.2 Preparation of test solutions

9.4.2.1 For determination in the range of 0,000 1 % to 0,01 %

Place the 10 g test portion in a 300 ml beaker and add approximately 20 ml of water and approximately 50 ml of concentrated nitric acid (9.2.1). Allow to dissolve slowly after covering the beaker with a watch glass. After complete dissolution, heat to boiling, then allow to cool to room temperature and transfer quantitatively to a 100 ml one-mark volumetric flask. Make up to the mark with water, mix well and transfer to a polyethylene bottle, which is then hermetically sealed when closed.

9.4.2.2 For determination in the range of 0,01 % to 0,1 %

Place the 1 g test portion in a 300 ml beaker and add approximately 10 ml of water and approximately 10 ml of concentrated nitric acid (9.2.1), covering the beaker with a watch glass. Continue as described in 9.4.2.1.

9.4.2.3 For determination in the range 0,1 % to 1 %

Proceed as in 9.4.2.2, but add approximately 50 ml of water and approximately 100 ml of concentrated nitric acid (9.2.1) to a 300 ml beaker, and transfer to a 1 000 ml one-mark volumetric flask.

9.4.3 Determination

9.4.3.1 Install the selected hollow-cathode or discharge lamp in the spectrometer and set up the instrument in accordance with the manufacturer's instructions. Adjust the orientation of the lamp in order to achieve maximum sensitivity. Select the spectral line depending on the element to be determined: 283,3 nm (or 217,0 nm) for lead, 228,8 nm for cadmium and 248,3 nm for iron.

9.4.3.2 Adjust the air/acetylene flame so that it is oxidizing; to do this, adjust the ratio of the feed rates of air and acetylene to at least 10, calculated at the same pressure.

9.4.3.3 Select the appropriate sensitivity scale on the apparatus.

9.4.3.4 Alternate measurements on calibration and test solutions.

9.4.3.5 Having determined the metal content in the two calibration solutions straddling the test solution, repeat two to five times the measurements on these three solutions to verify that the apparatus response is stable. Calculate the mean value of each set of measurements.

9.5 Expression of results

9.5.1 With apparatus giving readings in percentage absorption, convert these to relative absorbances.

9.5.2 Calculate the mass concentration, ρ, of the test solution, expressed in milligrams per litre, using Formula (6):

$$\rho = \rho_1 + \frac{A - A_1}{A_2 - A_1} \times (\rho_2 - \rho_1) \qquad (6)$$

where

ρ_1 and ρ_2 are the mass concentrations, in milligrams per litre, of the two calibration solutions straddling the test solution;

A_1 and A_2 are the relative absorbances of the calibration solutions;

A is the relative absorbance of the test solution.

9.5.3 Calculate the content, w, of the element to be determined (lead, cadmium or iron), expressed as a percentage by mass, using Formula (7):

$$w = \frac{\rho}{m_0 \times f} \qquad (7)$$

where

ρ is the mass concentration, in milligrams per litre, of the test solution, as calculated in 9.5.2;

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

f is a coefficient taking into account the dilution; if 9.4.2.1 or 9.4.2.2 is followed, $f = 100$; if 9.4.2.3 is followed, $f = 10$.

10 Determination of arsenic content

10.1 Principle

The arsenic in the test solution is reduced to the volatile hydride (arsine) using sodium borohydride. The arsine is decomposed using a hydrogen/nitrogen or hydrogen/argon flame, or a suitably heated tube. The arsenic is determined by atomic absorption spectrometry at a wavelength of 193,7 nm.

10.2 Reagents and materials

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

10.2.1 Nitric acid, CAS RN 7697-37-2, concentrated, approximately 68 % (mass fraction), $\rho \approx 1,42$ g/ml.

10.2.2 Sulfuric acid, CAS RN 7664-93-9, concentrated, approximately 96 % (mass fraction), $\rho \approx 1,84$ g/ml.

10.2.3 Sulfuric acid, CAS RN 7664-93-9, diluted 1 + 1.

Slowly add, while cooling, 1 part by volume of concentrated sulfuric acid (10.2.2) to 1 part by volume of water.

10.2.4 Hydrochloric acid, CAS RN 7647-01-0, concentrated, 37 % (mass fraction), $\rho \approx 1,19$ g/ml.

10.2.5 Metallic zinc, CAS RN 7440-66-6, 99,999 9 % (mass fraction) minimum purity.

10.2.6 Arsenic, CAS RN 7440-38-2, standard stock solution containing 0,25 g of arsenic/l.

Weigh, to the nearest 1 mg, 330 mg of arsenic trioxide (As_2O_3) into a 250 ml beaker and add 25 ml of a 100 g/l sodium hydroxide (NaOH) (CAS RN 1310-73-2) solution. Stir to dissolve, then add 50 ml of concentrated hydrochloric acid (10.2.4) and transfer quantitatively to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

1 ml of this solution contains 0,25 mg of arsenic.

10.2.7 Arsenic, standard solution containing 2,5 mg of arsenic/l.

Pipette 10 ml of the arsenic standard stock solution (10.2.6) into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Prepare this solution immediately before use.

1 ml of this solution contains 2,5 µg of arsenic.

10.2.8 Arsenic, calibration solutions.

Weigh, to the nearest 10 mg, 10 g of zinc (10.2.5) into each of five 1 l beakers. Add respectively 0 ml, 2 ml, 6 ml, 10 ml and 20 ml of the arsenic standard solution (10.2.7). Dissolve in approximately 50 ml of concentrated nitric acid (10.2.1). After complete dissolution, add 20 ml of dilute sulfuric acid (10.2.3). Heat gently to eliminate the nitric acid, then heat more vigorously to completely drive off all white fumes of sulfuric acid. Allow to cool, then add 50 ml of concentrated hydrochloric acid (10.2.4), cover the beaker with a watch glass and heat gently until complete dissolution. Allow to cool to room temperature and transfer quantitatively to five 100 ml one-mark volumetric flasks. Make up to the mark with water and mix well.

Prepare these solutions immediately before use.

These five calibration solutions contain, respectively, 0 µg, 50 µg, 150 µg, 250 µg and 500 µg of arsenic per litre, corresponding to 0 %, 0,000 05 %, 0,000 15 %, 0,000 25 % and 0,000 5 % of arsenic in the test portion when using the procedure specified in 10.4.

10.2.9 Potassium hydroxide, CAS RN 1310-58-3, 10 % (mass fraction) solution.

Dissolve 50 g of potassium hydroxide (KOH) pellets in 450 ml of water.

10.2.10 Sodium borohydride[4] ($NaBH_4$), CAS RN 16940-66-2, 0,2 g/l solution.

WARNING — Sodium borohydride is harmful if swallowed. Do not inhale dust. Avoid contact with eyes and skin.

Dissolve 2 g of sodium borohydride in 100 ml of water containing 5 ml of potassium hydroxide solution (10.2.9). Filter the solution, using vacuum suction, through a 0,45 µm membrane filter and store in a clean, stoppered glass bottle.

Keep this solution cool. Use it for no more than one week.

10.2.11 Sodium iodide, CAS RN 7681-82-5, 10 % (mass fraction) solution.

Dissolve 10 g of sodium iodide (NaI) crystals in 90 ml of water.

10.2.12 Hydrogen, CAS RN 1333-74-0, commercial grade, 99,99 % (volume fraction) minimum purity, in a cylinder.

10.2.13 Carrier gas.

Nitrogen (CAS RN 7727-37-9) minimum purity 99,999 % (volume fraction) [i.e. containing not more than 10 ppm (parts per million, volume fraction) of oxygen], or argon, analytical grade, can be used.

10.3 Apparatus

Ordinary laboratory apparatus and glassware, together with the following.

10.3.1 Flame atomic absorption spectrometer, suitable for measurements at a wavelength of 193,7 nm and fitted with the correct burner for a hydrogen/nitrogen or hydrogen/argon flame, or any suitable tube for carrying out the thermal decomposition of the arsine generated.

NOTE Electrically-heated silica tubes and hydride generation kits are available from manufacturers of commercial atomic absorption spectrometry equipment.

For flame operation, the spectrometer shall be capable of carrying out simultaneous background correction.

10.3.2 Arsenic electrodeless discharge tube.

10.3.3 Potentiometric chart recorder, having a full-scale response time of maximum 0,5 s in the 10 mV range.

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4) Also known as sodium tetrahydroborate.

NOTE A suitable peak-measuring device, such as an electronic integrator, can be used as an alternative.

10.3.4 Flowmeter, fitted with a stainless-steel needle valve and capable of working over the range of 1 l/min to 5 l/min.

10.3.5 Syringes, 10 ml capacity, with a 6 % (Luer) taper connector (see ISO 80369-7) for the needle.

10.3.6 Hypodermic needles, 0,7 mm nominal outside diameter and 0,39 mm bore with a 6 % (Luer) taper connector (see ISO 80369-7).

10.3.7 Hydride generation apparatus, the components of which are connected using ground-glass joints and flexible PVC tubing.

The gas outlet from the reaction vessel shall be connected directly to the auxiliary oxidizing gas inlet of the nebulizer. It is essential that the nebulizer overflow port and the nebulizer tube be completely sealed to prevent ingress of air to the flame.

A suitable generation apparatus is shown in Figure 2.

10.4 Procedure

10.4.1 Preparation of the calibration graph

Install the arsenic spectral source (10.3.2) in the spectrometer (10.3.1). Set up the instrument and the simultaneous background correction in accordance with the manufacturer's instructions, adjusting the monochromator to provide the maximum energy at the selected wavelength (193,7 nm).

Adjust the flow rates of the hydrogen and the carrier gas to produce, when ignited, a stable, transparent flame. Balance the output of the spectral source with that of the background corrector in accordance with the manufacturer's instructions to eliminate all nonspecific absorbances during passage of the hydride and associated gas through the flame.

If a recorder is used, it will be necessary to set the baseline and check for unwanted signal noise in the appropriate voltage range.

Pipette 20 ml of the most concentrated calibration solution (see 10.2.8) into the reaction vessel of the hydride generation apparatus (10.3.7). Connect the vessel to the auxiliary oxidizing gas inlet as shown in Figure 2 and allow the flow of carrier gas (10.2.13) to remove air from the reaction vessel for 10 s to 20 s at the predetermined optimum flow rate.

Inject quickly but steadily, by means of a 10 ml syringe (10.3.5), 5 ml of the sodium borohydride solution (10.2.10) and leave the syringe in position. Adjust, if necessary, the carrier gas flow rate and recorder range setting to produce a sharp peak of a height corresponding to approximately 90 % of the full-scale deflection for the most concentrated calibration solution.

NOTE 1 It can be necessary to repeat the initial test several times with the most concentrated calibration solution in order to optimize the characteristics of the system.

Repeat the procedure without further adjustment for each of the calibration solutions.

Plot a graph having the masses, in micrograms, of arsenic in the calibration solutions as abscissae and the corresponding peak heights, or, more precisely, the peak areas, reduced by that of the zero-calibration solution, as ordinates.

NOTE 2 Over this range, the graph will usually deviate only slightly from linearity.

10.4.2 Test portion

Weigh, to the nearest 1 mg, 10 g of the sample (m_0) into a 1 l beaker.

10.4.3 Preparation of the test solution

Dissolve the test portion in approximately 50 ml of concentrated nitric acid (10.2.1). After complete dissolution, add 20 ml of diluted sulfuric acid (10.2.3).

Heat gently to eliminate the nitric acid, then heat more vigorously to completely drive off all white fumes of sulfuric acid. Allow to cool, then add 50 ml of concentrated hydrochloric acid (10.2.4). Cover the beaker with a watch glass and heat gently until complete dissolution. Allow to cool to room temperature and transfer quantitatively to a 100 ml one-mark volumetric flask. Make up to the mark with water and mix well.

10.4.4 Determination

Pipette 20 ml of the test solution (10.4.3) into the reaction vessel of the hydride generation apparatus (10.3.7), followed by 10 ml of concentrated hydrochloric acid (10.2.4) and 0,5 ml of sodium iodide solution (10.2.11). Connect the vessel to the auxiliary oxidizing gas inlet as shown in Figure 2. Proceed as described in 10.4.1 and measure the peak reading corresponding to the arsenic present, taking care to correct for any reagent blank.

Repeat on a further 20 ml of the test solution and calculate the mean of the two readings. Compare this calculated peak reading with those obtained from the calibration solutions (10.2.8) and then repeat the procedure using the closest calibration solution to check for any possible variation in the instrument or the gas flow rates. If the reading obtained on the test solution is outside the calibration range, dilute the test solution (10.4.3) with water and repeat the procedure with 20 ml of the diluted test solution.

Determine from the calibration graph (10.4.1) the mass of arsenic (m_1) in 20 ml of the test solution.