

INTERNATIONAL STANDARD

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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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Reference number
ISO 3549:1995(E)

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 3549 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 3549:1976), which has been technically revised.

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Zinc dust pigments for paints — Specifications and test methods

1 Scope

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

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 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings.*

ISO 594-1:1986, *Conical fittings with a 6 % (Luer) taper for syringes, needles and certain other medical equipment — Part 1: General requirements.*

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

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

3 Definition

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

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

NOTE 1 Zinc dust pigments for paints may 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 complying with this International Standard, the essential requirements are specified in tables 1 and 2.

Table 1 — Composition of zinc dust pigment

Characteristic	Unit	Requirement	Test method
Total zinc content	% (m/m)	min. 98	See clause 7
Metallic zinc content	% (m/m)	min. 94	See clause 8
Lead (Pb) content	% (m/m)	max. 0,2	See clause 9
Cadmium (Cd) content	% (m/m)	max. 0,1	See clause 9
Iron (Fe) content	% (m/m)	max. 0,05	See clause 9
Arsenic (As) content	% (m/m)	max. 0,000 5	See clause 10
Chloride (Cl) content)	% (m/m)	max. 0,005	See clause 11
Matter insoluble in acid	% (m/m)	max. 0,05	See clause 12

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 % (m/m)	Test method
125	max. 0,01	See clause 6
90	max 0,1.	
45	max. 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.

4.3 The reference pigment shall also comply with the requirements given in tables 1 and 2.

5 Sampling

Take a representative sample of the product to be tested, as described in ISO 842.

WARNING — The sample shall on no account 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, 90 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, 90 µm and 125 µm, complying with 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 r/min to 25 r/min 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 better.

6.2.3 Timer (for example a stopwatch) according 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 and undamaged and is 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 0,01 g, 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.

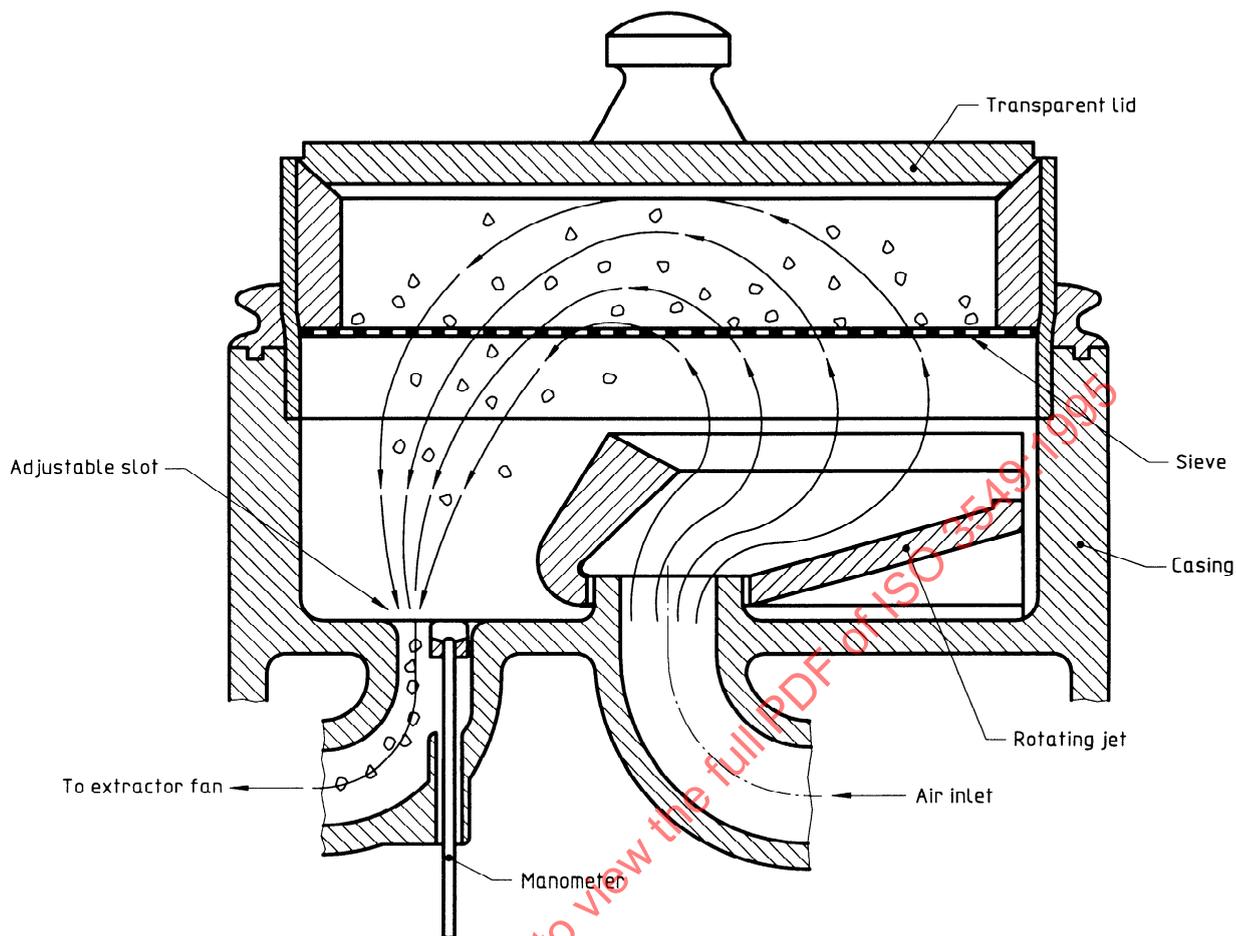


Figure 1 — Air-jet sieve apparatus

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 90 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 a percentage by mass, using the equation

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

where

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

m_1 is the mass, in grams, of the 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 90 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 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 defined in ISO 3696.

7.2.1 Hydrochloric acid, concentrated, approximately 38 % (m/m), $\rho \approx 1,19$ g/ml.

7.2.2 Hydrochloric acid, diluted 1 + 4.

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

7.2.3 Sulfuric acid, diluted 1 + 1.

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

7.2.4 Nitric acid, concentrated, approximately 68 % (m/m), $\rho \approx 1,42$ g/ml.

7.2.5 Ammonia solution, approximately 25 % (m/m), $\rho \approx 0,81$ g/ml.

7.2.6 Buffer solution.

Dissolve 200 g of hydroxylammonium chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in approximately 300 ml of water. Dissolve 28 g of sodium hydroxide in approximately 300 ml of water. Combine the two solutions, cool and dilute to 1 litre with water.

7.2.7 (Ethylenedinitrilo)tetraacetic acid (EDTA), disodium salt dihydrate, 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 litre. 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 (mass 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.

Calculate the zinc equivalent of the EDTA solution, $\rho(\text{Zn})$, expressed in grams per millilitre (i.e. the mass,

in grams, of zinc forming a complex with 1 ml of EDTA solution), using the equation

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

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 $\rho(\text{Zn})$, in grams per millilitre.

7.2.8 Xylenol orange, 1g/l indicator solution of the sodium salt in water.

7.2.9 Bromothymol blue, 1 g/l indicator solution in 96 % (V/V) 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, $w(\text{Zn})_t$, expressed as a percentage by mass, using the equation

$$w(\text{Zn})_t = \frac{1\,000 \times V_1 \times \rho(\text{Zn})}{m_1}$$

where

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

$\rho(\text{Zn})$ 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 % (m/m), 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 defined in ISO 3696.

8.2.1 Nitrogen, commercial grade, in a cylinder.

8.2.2 Orthophosphoric acid, approximately 85 % (m/m), $\rho \approx 1,71$ g/ml.

8.2.3 Sulfuric acid, diluted 1 + 19.

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

8.2.4 Copper(II) sulfate, solution.

Dissolve 200 g of copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 1 litre of water.

8.2.5 Iron(III) sulfate, saturated solution.

Dissolve, as far as possible, 330 g of iron(III) sulfate [$\text{Fe}_2(\text{SO}_4)_3$] in 1 litre of cold water. Heat until dissolution is complete. Allow to cool to room temperature, then filter.

8.2.6 Potassium permanganate, standard volumetric solution, $c(\text{KMnO}_4) \approx 0,06$ mol/l.

8.2.6.1 Preparation

Weigh 20 g of potassium permanganate (KMnO_4) into a 3-litre or 4-litre flask and add 2 litres 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 (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.

Calculate the concentration of the potassium permanganate solution, $c(\text{KMnO}_4)$, expressed in moles per litre, using the equation

$$c(\text{KMnO}_4) = \frac{2 \times m_0}{5 \times V_0 \times M_{\text{ox}}} \times 1\,000$$

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 ($M_{\text{ox}} = 134,00$ g/mol).

Carry out the titration three times and calculate the mean value of the concentration of the potassium permanganate solution, \bar{c} , in moles per litre.

Carry out this standardization before using the solution.

8.3 Procedure

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

8.3.1 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 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.

8.3.2 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 through it a stream of nitrogen (8.2.1) 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 ortho-phosphoric 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, $w(\text{Zn})_m$, expressed as a percentage by mass, using the equation

$$w(\text{Zn})_m = \frac{5 (V_1 - V_2) \times \bar{c} \times M_{\text{Zn}} \times 100}{2 m_1 \times 1000}$$

$$= 16,34 \times \frac{(V_1 - V_2) \times \bar{c}}{m_1}$$

where

\bar{c} is the mean 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 ($M_{\text{Zn}} = 65,37$ g/mol).

If the two results (duplicates) differ by more than 0,5 % (m/m), 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 defined in ISO 3696.

9.2.1 Nitric acid, concentrated, approximately 68 % (m/m), $\rho \approx 1,42$ g/ml.

9.2.2 Metallic lead, 99,99 % (m/m) minimum purity.

9.2.3 Metallic cadmium, 99,99 % (m/m) minimum purity.

9.2.4 Metallic iron, 99,99 % (m/m) minimum purity.

9.2.5 Metallic zinc, 99,999 9 % (m/m) minimum purity.

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

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 per litre.

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 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 and, 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 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 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 and 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, 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

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

Determination in the range 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 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 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 concentration, ρ , of the test solution, expressed in milligrams per litre, using the equation

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

where

ρ_1 and ρ_2 are the 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 the equation

$$w = \frac{\rho}{m_0 \times f}$$

where

ρ is the concentration of the test solution, in milligrams per litre, 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; $f = 100$ if 9.4.2.1 or 9.4.2.2 was followed, $f = 10$ if 9.4.2.3 was followed.

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 defined in ISO 3696.

10.2.1 Nitric acid, concentrated, approximately 68 % (m/m), $\rho \approx 1,42$ g/ml.

10.2.2 Sulfuric acid, concentrated, approximately 96 % (m/m), $\rho \approx 1,84$ g/ml.

10.2.3 Sulfuric acid, diluted 1 + 1.

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

10.2.4 Hydrochloric acid, concentrated, approximately 38 % (m/m), $\rho \approx 1,19$ g/ml.

10.2.5 Metallic zinc, 99,999 9 % (m/m) minimum purity.

10.2.6 Arsenic, standard stock solution containing 0,25 g of arsenic per litre.

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) 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 per litre.

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-litre 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 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, 10 % (*m/m*) solution.

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

10.2.10 Sodium borohydride¹⁾ (NaBH₄), 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, 10 % (*m/m*) solution.

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

10.2.12 Hydrogen, commercial grade, 99,99 % (V/V) minimum purity, in a cylinder.

10.2.13 Carrier gas.

Nitrogen, minimum purity 99,999 % (V/V) [i.e. containing not more than 10 ppm (V/V) 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 3 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 in the 10 mV range of not more than 0,5 s.

NOTE 4 A suitable peak-measuring device, such as an electronic integrator, may be used as an alternative.

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

10.3.5 Syringes, 10 ml capacity, with a 6 % (Luer) taper conical fitting (see ISO 594-1) for the needle.

1) Also known as sodium tetrahydroborate.

10.3.6 Hypodermic needles, 0,7 mm nominal outside diameter and 0,39 mm bore with a 6 % (Luer) taper conical fitting (see ISO 594-1).

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 non-specific absorbances during passage of the hydride and associated gas through the flame.

NOTE 5 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 6 It may 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 7 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-litre 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 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 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.