International Standard 3856/1

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Paints and varnishes — Determination of "soluble" metal content —

Part 1: Determination of lead content — Flame atomic absorption spectrometric method and dithizone spectrophotometric method

Peintures et vernis — Détermination de la teneur en métaux «solubles» — Partie 1: Détermination de la teneur en plomb — Méthode par spectrométrie d'absorption atomique dans la flamme et méthode spectrophotométrique à la dithizone

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Paints and varnishes — Determination of "soluble" metal content — Part 1: Determination of lead content — Flame atomic absorption spectrometric method and dithizone spectrophotometric method

0 Introduction

This International Standard is a part of ISO 3856, *Paints and varnishes — Determination of "soluble" metal content.*

1 Scope and field of application

This part of ISO 3856 describes two methods for the determination of the lead content of the test solutions, prepared according to ISO 6713 or other suitable International Standards.

The methods are applicable to paints having "soluble" lead contents in the range of about 0,05 to 5 % (*m*/*m*).

The flame atomic absorption spectrometric (AAS) method (clause 3) should be used as the referee method in cases of dispute. Other methods can be used by agreement between the interested parties. If a spectrophotometric method is agreed, the dithizone spectrophotometric method (clause 4) should be used.

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*[1]

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

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

ISO 3696, *Water for laboratory use — Specifications.*[2]

ISO 4800, *Laboratory glassware — Separating funnels and dropping funnels.*

ISO 6713, *Paints and varnishes — Preparation of acid extracts from paints in liquid or powder form.*

3 Flame atomic absorption spectrometric method

3.1 Principle

Aspiration of the test solution into an acetylene/air flame. Measurement of the absorption of the selected spectral line, emitted by a lead hollow-cathode or lead discharge lamp, in the region of 283,3 nm.

3.2 Reagents and materials

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

3.2.1 Hydrochloric acid, $c(\mathrm{HCl}) = 0{,}07$ mol/l.

Use the hydrochloric acid, identical to that used for the preparation of the test solutions in accordance with ISO 6713. (See 3.4.2.)

3.2.2 Acetylene, commercial grade, in a steel cylinder.

3.2.3 Compressed air.

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[1] At present at the stage of draft. (Partial revision of ISO/R 385-1964.)

[2] At present at the stage of draft.

3.2.4 Lead, standard stock solution containing 1 g of Pb per litre.

Either

a) transfer the contents of an ampoule of standard lead solution containing exactly 1 g of Pb into a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (3.2.1) and mix well;

or

b) weigh, to the nearest 1 mg, 1,598 g of lead nitrate [$Pb(NO_3)_2$] (previously dried for 2 h at 105 °C), dissolve in the hydrochloric acid (3.2.1) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the same hydrochloric acid and mix well.

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

3.2.5 Lead, standard solution containing 100 mg of Pb per litre.

Prepare this solution on the day of use.

Pipette 100 ml of the standard stock solution (3.2.4) into a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (3.2.1) and mix well.

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

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Flame atomic absorption spectrometer, suitable for measurements at a wavelength of 283,3 nm and fitted with a burner fed with acetylene and air.

3.3.2 Lead hollow-cathode lamp or **lead discharge lamp.**

3.3.3 Burette, of capacity 50 ml, complying with the requirements of ISO 385/1.

3.3.4 One-mark volumetric flasks, of capacity 100 ml, complying with the requirements of ISO 1042.

3.4 Procedure

3.4.1 Preparation of the calibration graph

3.4.1.1 Preparation of the standard matching solutions

Prepare these solutions on the day of use.

Into a series of six 100 ml one-mark volumetric flasks (3.3.4), introduce from the burette (3.3.3), respectively, the volumes of the standard lead solution (3.2.5) shown in the following table, dilute each to the mark with the hydrochloric acid (3.2.1) and mix well.

Standard matching solution No.	Volume of the standard lead solution (3.2.5)	Corresponding concentration of Pb in the standard matching solution
	ml	µg/ml
0 *	0	0
1	2,5	2,5
2	5	5
3	10	10
4	20	20
5	30	30

* Blank matching solution.

3.4.1.2 Spectrometric measurements

Install the lead spectral source (3.3.2) in the spectrometer (3.3.1) and optimize the conditions for the determination of lead. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 283,3 nm in order to obtain the maximum absorbance.

Adjust the flow of the acetylene (3.2.2) and of the air (3.2.3) according to the characteristics of the aspirator-burner, and ignite the flame. Set the scale expansion, if fitted, so that the standard matching solution No. 5 (see table) gives almost a full-scale deflection.

Aspirate into the flame each of the standard matching solutions (see 3.4.1.1) in ascending order of concentration, and repeat with the standard matching solution No. 4 to verify that the instrument has achieved stability. Aspirate water through the burner between each measurement, taking care to keep the rate of aspiration uniform.

3.4.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Pb contained in 1 ml of the standard matching solutions as abscissae and the corresponding values of the absorbances, reduced by the reading for the blank matching solution, as ordinates.

3.4.2 Test solutions

3.4.2.1 Pigment portion of the liquid paint and paint in powder form

Use the solutions obtained by the procedure described in sub-clause 8.2.3 or 8.3.2 of ISO 6713, as appropriate.

3.4.2.2 Liquid portion of the paint

Use the solutions obtained by the procedure described in sub-clause 9.3 of ISO 6713.

3.4.2.3 Other test solutions

Use the solutions obtained by other specified or agreed procedures (for example, by the procedure described in sub-clause 8.3.1.4 of ISO 6713).

3.4.3 Determination

Measure first the absorbance of the hydrochloric acid (3.2.1) in the spectrometer (3.3.1) after having adjusted it as described in 3.4.1.2. Then measure the absorbance of each test solution (3.4.2) three times and, afterwards, that of the hydrochloric acid again. Finally, re-determine the absorbance of standard matching solution No. 4 (see 3.4.1.1) in order to verify that the response of the apparatus has not changed. If the absorbance of a test solution is higher than that of the standard matching solution with the highest lead concentration, dilute the test solution appropriately (dilution factor F) with a known volume of the hydrochloric acid (3.2.1).

3.5 Expression of results

3.5.1 Calculations

3.5.1.1 Pigment portion of the liquid paint

Calculate the mass of "soluble" lead in the hydrochloric acid extract obtained by the method described in sub-clause 8.2.3 or 8.3.2 of ISO 6713, using the equation

$$m_0 = \frac{a_1 - a_0}{10^6} \times V_1 \times F_1$$

where

a_0 is the lead concentration, in micrograms per millilitre, of the blank test solution prepared by the method described in sub-clause 8.4 of ISO 6713;

a_1 is the lead concentration, in micrograms per millilitre, of the test solution obtained from the calibration graph;

F_1 is the dilution factor referred to in 3.4.3;

m_0 is the mass, in grams, of "soluble" lead in the hydrochloric acid extract;

V_1 is the volume, in millilitres, of the hydrochloric acid plus ethanol used for the extraction described in sub-clause 8.2.3 or 8.3.2.4 of ISO 6713 (assumed to be 77 ml or 502 ml respectively).

Calculate the "soluble" lead content of the pigment portion of the paint using the equation

$$c_{\text{Pb}_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where

c_{Pb_1} is the "soluble" lead content, of the pigment portion of the paint, expressed as a percentage by mass of the paint;

m_1 is the mass, in grams, of the test portion taken to prepare the solution described in sub-clause 8.2.3 or 8.3.2.4 of ISO 6713;

P is the pigment content of the liquid paint, expressed as a percentage by mass, obtained by the appropriate method described in clause 6 of ISO 6713.

3.5.1.2 Liquid portion of the paint

Calculate the mass of lead in the solution (extract), obtained by the method described in sub-clause 9.3 of ISO 6713, using the equation

$$m_2 = \frac{b_1 - b_0}{10^6} \times V_2 \times F_2$$

where

b_0 is the lead concentration, in micrograms per millilitre, of the blank test solution prepared by the method described in sub-clause 6.5 of ISO 6713;

b_1 is the lead concentration, in micrograms per millilitre, of the test solution obtained from the calibration graph;

F_2 is the dilution factor referred to in 3.4.3.;

m_2 is the mass, in grams, of lead in the liquid portion of the paint;

V_2 is the volume, in millilitres, of the solution obtained by the method described in sub-clause 9.3 of ISO 6713 (= 100 ml).

Calculate the lead content of the liquid portion of the paint, using the equation

$$c_{\text{Pb}_2} = \frac{m_2}{m_3} \times 10^2$$

where

c_{Pb_2} is the lead content of the liquid portion of the paint, expressed as a percentage by mass of the paint;

m_3 is the total mass, in grams, of paint comprising a "set" as described in sub-clause 6.4 of ISO 6713.

3.5.1.3 Liquid paint

Calculate the total "soluble" lead content of the liquid paint as the sum of the results obtained according to 3.5.1.1 and 3.5.1.2, thus

$$c_{\text{Pb}_3} = c_{\text{Pb}_1} + c_{\text{Pb}_2}$$

where c_{Pb_3} is the total "soluble" lead content of the paint, expressed as a percentage by mass.

3.5.1.4 Paint in powder form

The total "soluble" lead content of the paint in powder form is obtained by appropriate modification of the calculations given in 3.5.1.1.

3.5.1.5 Other test solutions

If the test solutions were prepared by methods other than those given in ISO 6713 (see 3.4.2.3), it will be necessary to modify the equations for the calculation of lead content given in 3.5.1.1 and 3.5.1.2.

3.5.2 Precision

No precision data are currently available.

4 Dithizone spectrophotometric method

4.1 Principle

Extraction of the lead from the test solution with a solution of dithizone in 1,1,1-trichloroethane. Spectrophotometric measurement of the red colour of the lead dithizonate at a wavelength of about 520 nm.

4.2 Reagents

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

4.2.1 Hydrochloric acid, $c(\mathrm{HCl}) = 0{,}07$ mol/l.

Use the hydrochloric acid, identical to that used for the preparation of the test solutions in accordance with ISO 6713. (See 4.4.2.)

4.2.2 Buffer solution.

Dissolve 3 g of potassium cyanide, 6 g of sodium metabisulfite and 5 g of ammonium citrate in about 200 ml of water, add 325 ml of ammonia solution (ϱ approximately 0,880 g/ml) and dilute to 1 litre with water.

WARNING — Note should be taken of the extreme toxicity of potassium cyanide and its solutions.

4.2.3 Hydroxylammonium chloride, 20 % (m/m) solution.

Dissolve 20 g of hydroxylammonium chloride in about 75 ml of water and make up to 100 ml.

WARNING — Hydroxylammonium chloride is toxic, corrosive and irritant. Avoid contact with eyes and skin.

4.2.4 1,1,1-trichloroethane, free from inhibitors.

4.2.5 Dithizone, stock solution.

Dissolve 40 mg of dithizone in 100 ml of the 1,1,1-trichloroethane (4.2.4).

Store in a refrigerator at 4 °C or below. Discard 7 days after preparation.

4.2.6 Dithizone, working solution.

Prepare this solution on the day of use.

Dilute 10 ml of the dithizone stock solution (4.2.5) to 100 ml with the 1,1,1-trichloroethane (4.2.4).

4.2.7 Lead, standard stock solution containing 1 g of Pb per litre.

Either

a) transfer the contents of an ampoule of standard lead solution containing exactly 1 g of Pb into a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (4.2.1) and mix well;

or

b) weigh, to the nearest 1 mg, 1,598 g of lead nitrate $[\mathrm{Pb(NO_3)_2}]$ (previously dried for 2 h at 105 °C), dissolve in the hydrochloric acid (4.2.1) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the same hydrochloric acid and mix well.

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

4.2.8 Lead, standard solution containing 10 mg of Pb per litre.

Prepare this solution on the day of use.

Pipette 10 ml of the standard stock solution (4.2.7) into a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (4.2.1) and mix well.

1 ml of this standard solution contains 10 µg of Pb.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Spectrophotometer, suitable for measurements at a wavelength of about 520 nm, fitted with cells of optical path length 5 mm.

4.3.2 Separating funnels, of capacity 50 ml, complying with the requirements of ISO 4800.

4.3.3 Pipette, of capacity 10 ml, complying with the requirements of ISO 648.

4.3.4 Burette, of capacity 10 ml, complying with the requirements of ISO 385/1.

4.3.5 One-mark volumetric flasks, of capacity 100 ml, complying with the requirements of ISO 1042.

4.4 Procedure

4.4.1 Preparation of the calibration graph

4.4.1.1 Preparation of standard colorimetric solutions

Prepare these solutions on the day of use.

Transfer 15 ml portions of the buffer solution (4.2.2) to each of a series of six 50 ml separating funnels (4.3.2), followed by 1 ml of the hydroxylammonium chloride solution (4.2.3) and 5 ml of the dithizone solution (4.2.6). Stopper the funnels and shake vigorously for about 30 s. Allow to stand until the layers separate and then run off and discard the lower layers. Dry the insides of the stems of the separating funnels with strips of filter paper.