
International Standard



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● **Paints and varnishes — Determination of “soluble” metal content —**

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

STANDARD PREVIEW

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

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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 developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

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.

International Standard ISO 3856/1 was developed by Technical Committee ISO/TC 35, *Paints and varnishes*.

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This second edition was submitted directly to the ISO Council, in accordance with clause 6.11.2 of part 1 of the Directives for the technical work of ISO. It cancels and replaces the first edition (i.e. ISO 3856/1-1980), which had been approved by the member bodies of the following countries :

Australia	Iran	Poland
Austria	Ireland	Romania
Brazil	Israel	South Africa, Rep. of
Bulgaria	Italy	Sweden
Egypt, Arab Rep. of	Kenya	Switzerland
France	Korea, Rep. of	Turkey
Germany, F. R.	Mexico	United Kingdom
India	Norway	USSR

The member body of the following country expressed disapproval of the document on technical grounds :

Canada

Paints and varnishes — Determination of “soluble” metal content —

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

0 Introduction

This document is a part of ISO 3856, *Paints and varnishes — Determination of “soluble” metal content.*

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

ISO 6713, *Paints and varnishes — Preparation of acid extracts from paints in liquid and powder form.*²⁾

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1 Scope and field of application

This part of ISO 3856 specifies 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” metal contents in the range of about 0,05 to 5 % (*m/m*).

The flame atomic absorption spectroscopic (AAS) method (clause 3) should be used as the reference method. Other methods can be used by agreement between the interested parties. If a molecular absorption method is agreed, the dithizone spectrometric method (clause 4) should be used. In case of dispute, the AAS method 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.*

3 Flame atomic absorption spectroscopic 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 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 distilled water or water of equivalent purity.

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

Use the identical hydrochloric acid solution as used for the preparation of the test solutions.

3.2.2 Acetylene, in a steel cylinder.

3.2.3 Compressed air.

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

2) At present at the stage of draft. (Revision of ISO 6713-1980.)

3.2.4 Lead, standard solution corresponding to 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 solution (3.2.1), and mix well.

or

b) weigh, to the nearest 1 mg, 1,598 g of lead nitrate, dissolve in the hydrochloric acid solution (3.2.1) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the same hydrochloric acid solution, and mix well.

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

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

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

Prepare this solution on the day of use.

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.

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

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

Prepare these solutions on the day of use.

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

* Blank test on reagents for calibration graph.

3.4.1.2 Spectroscopic measurements

Install the lead hollow-cathode lamp (3.3.2) in the spectrometer (3.3.1) and leave the apparatus switched on for the time necessary to achieve stability. Adjust the lamp current, the attenuation and the slit, to suit the characteristics of the apparatus. Adjust the wavelength to the region of 283,3 nm in order to obtain the maximum absorbance. Adjust the pressures of the acetylene (3.2.2) and of the air (3.2.3) according to the characteristics of the aspirator-burner. Aspirate the series of standard matching solutions (3.4.1.1) into the flame and measure the absorbance for each. Aspirate water through the burner after each measurement. Take care to keep the rate of aspiration constant throughout the preparation of the calibration graph.

3.4.1.3 Plotting the 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 value for the blank test solution, as ordinates.

3.4.2 Test solutions

3.4.2.1 Pigments and extenders

Use the solution obtained by the procedure specified in sub-clause 7.2.2 of ISO 6713.

3.4.2.2 Liquid portion of the paint

Use the solution obtained by the procedure specified in clause 8 of ISO 6713.

3.4.2.3 Other test solutions

Use the solution obtained by other specified or agreed procedures.

3.4.3 Determination

Measure the absorbance of each test solution (3.4.2) three times in the apparatus after having adjusted it as specified in 3.4.1.2. Measure first the absorbance of the hydrochloric acid solution (3.2.1), then that of the test solution and afterwards that of the hydrochloric acid solution again. Finally, re-determine the absorbances of the standard matching solutions

(3.4.1.1) in order to verify that the adjustment 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 with a known volume of the hydrochloric acid solution (3.2.1).

3.5 Expression of results

3.5.1 Calculations

3.5.1.1 Pigments and extenders

The mass of "soluble" lead in the hydrochloric acid extract obtained by the method specified in sub-clause 7.2.2 of ISO 6713 is given by the equation

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

where

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

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

a_0 is the lead concentration, in micrograms per millilitre, of the blank test solution prepared by the method specified in sub-clause 7.3 of ISO 6713;

V_1 is the volume, in millilitres, of the hydrochloric acid solution plus ethanol used for the extraction specified in sub-clause 7.2.2 of ISO 6713 (assumed to be 502 ml);

F_1 is the dilution factor referred to in 3.4.3.

The "soluble" lead content of the pigment and extender portion of the paint, is given by the equation

$$c_{Pb1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where

c_{Pb1} is the "soluble" lead content, of the pigment and extender portion of the paint, expressed as a percentage by mass of the paint;

P is the pigment and extender content of the paint, expressed as a percentage by mass, obtained by the appropriate method specified in clause 6 of ISO 6713;

m_1 is the mass, in grams, of the test portion taken to prepare the solution specified in sub-clause 7.2.2 of ISO 6713.

3.5.1.2 Liquid portion of the paint

The mass of lead in the solution (extract), obtained by the method specified in clause 8 of ISO 6713, is given by the equation

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

where

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

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

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

V_2 is the volume, in millilitres, of the solution (100 ml) obtained by the method specified in clause 8 of ISO 6713;

F_2 is the dilution factor referred to in 3.4.3.

The lead content of the liquid portion of the paint is given by the equation

$$c_{Pb2} = \frac{m_2}{m_3} \times 10^2$$

where

c_{Pb2} 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 specified in sub-clause 6.4 of ISO 6713.

3.5.1.3 Paint

The total "soluble" lead content of the paint is given by the sum of the results obtained according to 3.5.1.1 and 3.5.1.2, thus

$$c_{Pb3} = c_{Pb1} + c_{Pb2}$$

where c_{Pb3} is the total "soluble" lead content of the paint, expressed as a percentage by mass.

3.5.1.4 Other test solutions

If the test solutions were prepared by methods other than that given in ISO 6713 (see 3.4.2.3), it is 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 spectrometric method

4.1 Principle

Extraction of the lead from the test solution with a solution of dithizone in 1,1,1-trichloroethane. Spectrometric 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 distilled water or water of equivalent purity.

4.2.1 Hydrochloric acid, 0,07 mol/l solution.

Use the identical hydrochloric acid solution as used for the preparation of the test solutions.

4.2.2 Buffer solution.

Dissolve 3 g of potassium cyanide, 6 g of sodium metabisulphite 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.

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

Prepare this solution on the day of use.

4.2.7 Lead, standard solution corresponding to 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 solution (4.2.1) and mix well,

or

b) weigh, to the nearest 1 mg, 1,598 g of lead nitrate, dissolve in the hydrochloric acid solution (4.2.1) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the same hydrochloric acid solution, and mix well.

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

4.2.8 Lead, standard solution corresponding to 20 mg of Pb per litre.

Pipette 20 ml of the standard lead solution (4.2.7) into a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid solution (4.2.1) and mix well.

Prepare this solution on the day of use.

1 ml of this standard solution contains 20 µg of Pb.

4.2.9 Lead, standard solution corresponding to 2 mg of Pb per litre.

Pipette 25 ml of the standard lead solution (4.2.8) into a 250 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid solution (4.2.1) and mix well.

Prepare this solution on the day of use.

1 ml of this standard solution contains 2 µg of Pb.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Spectrometer, suitable for measurements at a wavelength of about 520 nm, fitted with cells of optical path length 10 or 20 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 for spectrometric measurements in cells of optical path length 10 or 20 mm

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 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.

Introduce from the 10 ml burette (4.3.4) the volumes of the standard lead solution (4.2.9) shown in the following table, into the funnels and then, from a pipette (4.3.3), 10 ml of the 1,1,1-trichloroethane (4.2.4). Stopper the funnels and shake vigorously for 30 s. Allow the layers to separate and run off the lower layers through small funnels fitted with dry filter papers to absorb any droplets of water, collecting the solutions in separate spectrometer cells (4.3.1).

Standard colorimetric solution No.	Standard lead solution (4.2.9)	Corresponding concentration of Pb in colorimetric solution
	ml	µg/ml
0*	0	0
1	1	0,2
2	2	0,4
3	3	0,6
4	4	0,8
5	5	1,0

* Compensation solution.

4.4.1.2 Spectrometric measurements

Measure the absorbances of the standard colorimetric solutions (4.4.1.1) with the spectrometer (4.3.1) at the wavelength of maximum absorption (about 520 nm) against 1,1,1-trichloroethane (4.2.4) in the reference cell. Before each measurement, rinse the cells with the standard colorimetric solution. Deduct the absorbance of the compensation solution from those of the other standard colorimetric solutions.

4.4.1.3 Plotting the graph

Plot a graph having the masses, in micrograms, of Pb contained in 1 ml of the standard colorimetric solutions as abscissae, and the corresponding values of absorbance as ordinates. If the procedure has been carried out correctly, the calibration graph should be a straight line.

4.4.2 Test solutions

4.4.2.1 Pigments and extenders

Use the solution obtained by the procedure specified in sub-clause 7.2.2 of ISO 6713.

4.4.2.2 Liquid portion of the paint

Use the solution obtained by the procedure specified in clause 8 of ISO 6713.

4.4.2.3 Other test solutions

Use the solution obtained by other specified or agreed procedures.

4.4.3 Determination

Transfer by means of the 10 ml burette (4.3.4) a volume of the test solution (4.4.2) containing 0,5 to 1,0 µg of Pb to a 50 ml separating funnel, add 1 ml of the hydroxylammonium chloride solution (4.2.3), swirl and allow to stand for a few minutes. Add 15 ml of the buffer solution (4.2.2) followed by 5 ml of the dithizone solution (4.2.6). Stopper the funnel and shake vigorously for 30 s. Allow the layers to separate and run off the lower layer through a small funnel fitted with a dry, filter paper to absorb any droplets of water, collecting the solution in a spectrometer cell (4.3.1).

Measure the absorbance by the procedure specified in 4.4.1.2.

4.5 Expression of results

4.5.1 Calculations

4.5.1.1 Pigments and extenders

The mass of "soluble" lead in the hydrochloric acid extract, obtained by the method specified in sub-clause 7.2.2 of ISO 6713, is given by the equation

$$m_0 = \frac{10(a_1 - a_0)}{10^6} \times \frac{V_1}{V_3} = \frac{(a_1 - a_0) V_1}{V_3} \times 10^{-5}$$

where

a_1, a_0, m_0, V_1 are as defined in 3.5.1.1;

V_3 is the volume, in millilitres, of the aliquot portion of the hydrochloric acid plus ethanol extract taken for the test.

The "soluble" lead content of the pigment and extender portion of the paint is given by the equation

$$c_{Pb1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where c_{Pb1}, P, m_1 are as defined in 3.5.1.1.

4.5.1.2 Liquid portion of the paint

The mass of lead in the solution (extract), obtained by the method specified in clause 8 of ISO 6713, is given by the equation

$$m_2 = \frac{10(b_1 - b_0)}{10^6} \times \frac{V_2}{V_4} = \frac{(b_1 - b_0) V_2}{V_4} \times 10^{-5}$$

where

m_2, b_1, b_0, V_2 are as defined in 3.5.1.2;

V_4 is the volume, in millilitres, of the aliquot portion of the solution taken for the test.

The lead content of the liquid portion of the paint is given by the equation

$$c_{Pb_2} = \frac{m_2}{m_3} \times 10^2$$

where c_{Pb_2} , m_3 are as defined in 3.5.1.2.

4.5.1.3 Paint

The total "soluble" lead content of the paint is given by the sum of the results obtained according to 4.5.1.1 and 4.5.1.2, thus

$$c_{Pb_3} = c_{Pb_1} + c_{Pb_2}$$

where c_{Pb_3} is as defined in 3.5.1.3.

4.5.1.4 Other test solutions

If the test solutions were prepared by methods other than that given in ISO 6713 (see 4.4.2.3), it is necessary to modify the equations for the calculation of lead content given in 4.5.1.1 and 4.5.1.2.

4.5.2 Precision

No precision data are currently available.

5 Test report

The test report shall include at least the following information :

- a) the type and identification of the product tested;
- b) a reference to this International Standard (ISO 3856/1);
- c) the method for the separation of the solid portion of the product under test according to ISO 6713, clause 6 (method A, B or C);
- d) the solvent or the solvent mixture used for the extraction;
- e) the method of determination (AAS or dithizone spectrometric) used;
- f) any deviation, by agreement or otherwise, from the test procedure specified;
- g) the results of the tests, expressed as a percentage by mass of the product, i.e. the "soluble" lead content of the pigment and extender, the lead content of the liquid portion of the paint and the total "soluble" lead content of the paint;
- h) the date of the test.

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