TC 35

International Standard ISO 3856/1

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

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

Part 1 : Determination of lead content — Flame atomic absorption spectroscopic 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 spectroscopie d'absorption atomique dans la flamme et méthode spectrophotométrique à la dithizone

First edition — 1980-02-01

UDC 667.6 : 543.422 : 546.815 **Ref. No. ISO 3856/1-1980 (E)**

Descriptors : paints, varnishes, printing inks, chemical analysis, determination of content, soluble matter, metals, extraction analysis, test specimen conditioning.

Price based on 6 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (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 set up 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 (formerly DIS 3856/6) was developed by Technical Committee ISO/TC 35, *Paints and varnishes*, and was circulated to the member bodies in April 1978.

It has been approved by the member bodies of the following countries :

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

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

Canada

Printed in Switzerland

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

0 Introduction

This document 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 specifies two methods for the determination of the lead content of the test solutions, prepared according to ISO 6713 or other suitable International Standards[1]. 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 spectrophotometric method is agreed, the dithizone method (clause 4) should be used. In case of dispute, the AAS method should be used.

2 References

ISO/R 385, *Burettes.*

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

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

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

ISO 6713, *Paints and varnishes — Preparation of acid extracts from liquid paints.*[1]

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.

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, 0,07 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.

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.

---

[1] The preparation of acid extracts from dried films and powder coatings will form the subject of a future International Standard.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Flame atomic absorption spectrometer, 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/R 385.

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 the 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 in 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 of 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, redetermine 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 above.

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

$$c_{Pb_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where

c_{Pb_1} is the "soluble" lead content, of the pigment 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 acid 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 acid 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 above.

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} 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

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

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

3.5.1.4 Other test solutions

If the test solutions were prepared by other methods 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 above.

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 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.

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 Spectrophotometer, 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/R 385.

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 spectrophotometric 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 collect droplets of water, collecting the solutions in separate spectrophotometer cells (4.3.1).

Colorimetric solution No.	Standard lead solution (4.2.9)	Corresponding concentration of Pb in the 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.