International Standard ISO 3856/4

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Paints and varnishes — Determination of "soluble" metal content — Part 4 : Determination of cadmium content — Flame atomic absorption spectroscopic method and polarographic method

Peintures et vernis — Détermination de la teneur en métaux «solubles» — Partie 4 : Détermination de la teneur en cadmium — Méthode par spectroscopie d'absorption atomique dans la flamme et méthode polarographique

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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.

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

Australia	Iran	Romania
Austria	Ireland	South Africa, Rep. of
Brazil	Israel	Sweden
Bulgaria	Italy	Switzerland
Canada	Kenya	Turkey
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Paints and varnishes — Determination of "soluble" metal content — Part 4 : Determination of cadmium content — Flame atomic absorption spectroscopic method and polarographic 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 cadmium content of the test solutions prepared according to ISO 6713 or 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 method (AAS) (clause 3) should be used as the reference method. Other methods can be used by agreement between the interested parties. A polarographic method is given in clause 4. 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 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 (228,8 nm) emitted by a cadmium 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 Cadmium, standard solution corresponding to 1 g of Cd per litre.

Prepare the solution in one of the following ways :

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

b) Weigh, to the nearest 1 mg, a mass of a water-soluble cadmium salt of defined purity containing exactly 1 g of Cd, 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.

c) Weigh, to the nearest 1 mg, exactly 1 g of cadmium metal, dissolve it in the minimum of concentrated hydrochloric acid solution (ϱ = 1,18 g/ml) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid solution (3.2.1), and mix well.

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

1) The preparation of acid extracts from dried films and powder coatings will form the subject of future International Standards.

3.2.5 Cadmium, standard solution corresponding to 10 mg of Cd per litre.

Pipette 10 ml of the standard cadmium 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 10 µg of Cd.

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 Cadmium hollow-cathode lamp.

3.3.3 Burette, of capacity 10 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 five 100 ml one mark volumetric flasks (3.3.4), the volumes of the standard cadmium 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 cadmium solution (3.2.5)	Corresponding concentration of Cd in matching solution
	ml	µg/ml
0*	0	0
1	0,5	0,05
2	1,0	0,1
3	2,0	0,2
4	4,0	0,4

* Blank test on reagents for calibration graph.

3.4.1.2 Spectroscopic measurements

Install the cadmium 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 228,8 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 Cd 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 7.2.1 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 test 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 cadmium 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" cadmium in the hydrochloric acid extract, obtained by the method specified in sub-clause 7.2.1 of ISO 6713, is given by the equation

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

where

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

a_1 is the cadmium 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" cadmium in the hydrochloric acid extract;

V_1 is the volume, in millilitres, of the hydrochloric acid solution plus ethanol used for the extraction specified in sub-clause 7.2.1 of ISO 6713 (assumed to be 77 ml).

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

$$c_{Cd_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2}$$

$$= \frac{m_0 \times P}{m_1}$$

where

c_{Cd_1} is the "soluble" cadmium content of the pigment and extender 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 solutions specified in sub-clause 7.2.1 of ISO 6713;

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.

3.5.1.2 Liquid portion of the paint

The mass of cadmium 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

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

b_1 is the cadmium 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 cadmium in the solution obtained according to clause 8 of ISO 6713;

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

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

$$c_{Cd_2} = \frac{m_2}{m_3} \times 10^2$$

where

c_{Cd_2} is the cadmium 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" cadmium 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

$$c_{Cd_3} = c_{Cd_1} + c_{Cd_2}$$

where c_{Cd_3} is the total "soluble" cadmium 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 will be necessary to modify the equations for the calculation of cadmium content given in 3.5.1.1 and 3.5.1.2.

3.5.2 Precision

No precision data are currently available.

4 Polarographic method

4.1 Principle

Electrolysis of the test solution on a polarographic cell and measurement of the corresponding height of the potential step.

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 Sulphuric acid, approximately 98 % (m/m) solution, ϱ approximately 1,84 g/ml.

4.2.2 Hydrogen peroxide, solution, 30 % (m/m).

4.2.3 Base solution

Dissolve 27 g of ammonium chloride and 0,05 g of gelatine in water and add 32 ml of ammonia solution, approximately 33 % (m/m) solution, ϱ approximately 0,880 g/ml. Dilute the solution to 500 ml with water, and mix well.

4.2.4 Nitrogen, in a steel cylinder.

4.2.5 Cadmium, standard solution corresponding to 1 g of Cd per litre.

Prepare the solution in one of the following ways :

a) Transfer the contents of an ampoule of standard cadmium solution containing exactly 1 g of Cd into a 1 000 ml one-mark volumetric flask, dilute to the mark with water, and mix well.

b) Weigh, to the nearest 1 mg, a mass of a water-soluble cadmium salt of defined purity containing exactly 1 g of Cd, dissolve in water in a 1 000 ml one-mark volumetric flask, dilute to the mark with water, and mix well.

c) Weigh, to the nearest 1 mg, exactly 1 g of cadmium metal, dissolve it in the minimum of concentrated hydrochloric acid solution (ϱ = 1,18 g/ml) in a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

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

4.2.6 Cadmium, standard solution corresponding to 10 mg of Cd per litre.

Pipette 10 ml of the standard cadmium solution (4.2.5) into a 1 000 ml one-mark volumetric flask, dilute to the mark with water, and mix well.

Prepare this solution on the day of use.

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

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Suitable polarograph with recorder

4.3.2 Measuring electrode : Dropping mercury electrode

4.3.3 Reference electrode : Platinum electrode or saturated calomel electrode.

4.3.4 Auxiliary electrode : Tungsten electrode or platinum electrode.

4.3.5 Gas washing bottle.

4.3.6 Pipette, of suitable capacity, complying with the requirements of ISO 648.

4.3.7 Burette, of capacity 10 ml, complying with the requirements of ISO/R 385.

4.3.8 One-mark volumetric flasks, of capacity 25 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 the standard matching solutions

Introduce from the burette (4.3.7), into a series of seven beakers, the volumes of the standard cadmium solution (4.2.6) shown in the following table.

Standard matching solution No.	Standard cadmium solution (4.2.6)	Corresponding concentration of Cd in matching solution
	ml	µg/ml
0*	0	0
1	1,0	0,4
2	2,0	0,8
3	4,0	1,6
4	6,0	2,4
5	8,0	3,2
6	10	4,0

* Blank test on reagents for calibration graph.

Treat the contents of each beaker as follows :

Add 2 ml of the sulphuric acid solution (4.2.1) and evaporate until white fumes are evolved. If the residue is coloured, oxidize it with the hydrogen peroxide solution (4.2.2) until it is colourless. Evaporate the sulphuric acid completely and dissolve the residue in the base solution (4.2.3). Transfer to a 25 ml one-mark volumetric flask (4.3.8), make up to the mark with the base solution and mix well.

Prepare this solution on the day of use.

4.4.1.2 Polarographic measurements

Transfer the standard matching solutions (4.4.1.1) separately into the polarographic cell. De-aerate each solution by passing nitrogen (4.2.4) through it, after having first passed the nitrogen through the gas washing bottle (4.3.5) containing the base solution (4.2.3).

Electrolyze the solution in the cell at a voltage of between $-0,5$ and $-2,5$ V at a sensitivity of 2×10^{-8} A/mm. The half-step potential is between $-1,45$ and $-1,50$ V. Measure the step height.