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 spectrometric method and polarographic method

Peintures et vernis — Détermination de la teneur en métaux «solubles» — Partie 4: Détermination de la teneur en cadmium — Méthode par spectrométrie 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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 3856/4 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

ISO 3856/4 was first published in 1980. This second edition cancels and replaces the first edition, of which it constitutes a thorough revision.

Paints and varnishes — Determination of "soluble" metal content — Part 4: Determination of cadmium content — Flame atomic absorption spectrometric method and polarographic 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 cadmium content of the test solutions prepared according to ISO 6713 or other suitable International Standards.

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

The flame atomic absorption spectrometric method (AAS) (clause 3) should be used as the referee method in cases of dispute. Other methods can be used by agreement between the interested parties. A polarographic method is given in clause 4.

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 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 cadmium hollow-cathode or cadmium discharge lamp, in the region of 228,8 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(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.

3.2.4 Cadmium, standard stock solution containing 1 g of Cd per litre.

Either

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 (3.2.1) and mix well;

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

2) At present at the stage of draft.

or

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 (3.2.1) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the same hydrochloric acid and mix well;

or

c) weigh, to the nearest 1 mg, exactly 1 g of cadmium metal, dissolve it in the minimum of concentrated hydrochloric acid (ϱ approximately 1,18 g/ml) in 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 stock solution contains 1 mg of Cd.

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

Prepare this solution on the day of use.

Pipette 10 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 10 µg of Cd.

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Flame atomic absorption spectrometer, suitable for measurement at a wavelength of 228,8 nm and fitted with a burner fed with acetylene and air.

3.3.2 Cadmium hollow-cathode lamp or **cadmium discharge lamp.**

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

* Blank matching solution.

3.4.1.2 Spectrometric measurements

Install the cadmium spectral source (3.3.2) in the spectrometer (3.3.1) and optimize the conditions for the determination of cadmium. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 228,8 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. 4 (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. 3 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 Cd 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 subclause 8.2.3 of ISO 6713.

3.4.2.2 Liquid portion of the paint

Use the solutions obtained by the procedure described in subclause 9.3 of ISO 6713.

3.4.2.3 Other test solutions

Use the test solutions obtained by other specified or agreed procedures.

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. 3 (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 cadmium 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" cadmium in the hydrochloric acid extract, obtained by the method described in sub-clause 8.2.3 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 cadmium 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 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 plus ethanol used for the extraction described in sub-clause 8.2.3 of ISO 6713 (assumed to be 77 ml).

Calculate the "soluble" cadmium content of the pigment portion of the paint using 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 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 described in sub-clause 8.2.3 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 cadmium 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 cadmium 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 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 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 cadmium content of the liquid portion of the paint, using 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 described in sub-clause 6.4 of ISO 6713.

3.5.1.3 Liquid paint

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

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

where c_{Cd_3} is the total "soluble" cadmium content of the paint, expressed as a percentage by mass.

3.5.1.4 Paint in powder form

The total "soluble" cadmium 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 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 in 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 water of at least grade 3 purity according to ISO 3696.

4.2.1 Sulfuric acid, approximately 98 % (*m/m*) (ϱ approximately 1,84 g/ml).

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

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, commercial grade, in a steel cylinder.

4.2.5 Cadmium, standard stock solution containing 1 g of Cd per litre.

Either

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;

or

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;

or

c) weigh, to the nearest 1 mg, exactly 1 g of cadmium metal, dissolve it in the minimum of concentrated hydrochloric acid (ϱ approximately 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 stock solution contains 1 mg of Cd.

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

Prepare this solution on the day of use.

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

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 385/1.

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

Prepare these solutions on the day of use.

Into a series of seven 100 ml beakers, introduce from the burette (4.3.7), respectively, the volumes of the standard cadmium solution (4.2.6) shown in the following table.

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

* Blank matching solution.

Treat the contents of each beaker as follows:

Add 2 ml of the sulfuric acid (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 sulfuric 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.

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.

4.4.1.3 Calibration graph

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

NOTE — This calibration graph is suitable for "soluble" cadmium contents, in the solid portion of the product tested, of between 0,015 and 0,15 % (m/m). If the cadmium content is between 0,001 5 and 0,015 % (m/m), a separate calibration graph will be required. Cadmium contents lower than 0,001 5 % (m/m) cannot be detected by the polarographic method.

4.4.2 Test solutions

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

Use the solutions obtained by the procedure described in subclause 8.2.3 of ISO 6713.

4.4.2.2 Liquid portion of the paint

Use the solutions obtained by the procedure described in subclause 9.3 of ISO 6713.

4.4.2.3 Other test solutions

Use the solutions obtained by other specified or agreed procedures.

4.4.3 Determination

Introduce into beakers accurately measured volumes of each of the test solutions (4.4.2) such that the resulting step height will be within the calibration range.

Treat the contents of each beaker as follows:

Add 2 ml of the sulfuric acid (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 sulfuric 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. Transfer the solution to the polarographic cell, de-aerate, electrolyze and measure the step height as described in 4.4.1.2.

4.5 Expression of results

4.5.1 Calculations

4.5.1.1 Pigment portion of the liquid paint

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

$$m_0 = \frac{a_1 - a_0}{10^6} \times \frac{V_1}{V_3} \times 25$$

where

a_0, a_1, m_0 and 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 taken for the test.

Calculate the "soluble" cadmium content of the pigment portion of the paint, using 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}, m_1 and P are as defined in 3.5.1.1.

4.5.1.2 Liquid portion of the paint

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

$$m_2 = \frac{b_1 - b_0}{10^6} \times \frac{V_2}{V_4} \times 25$$

where

b_0, b_1, m_2 and 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.

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

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

where c_{Cd_2} and m_3 are as defined in 3.5.1.2.

4.5.1.3 Liquid paint

Calculate the total "soluble" cadmium content of the liquid paint as the sum of the results obtained according to 4.5.1.1 and 4.5.1.2, thus

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

where c_{Cd_3} is as defined in 3.5.1.3.

4.5.1.4 Paint in powder form

The total "soluble" cadmium content of the paint in powder form is obtained by appropriate modification of the calculations given in 4.5.1.1.

4.5.1.5 Other test solutions

If the test solutions were prepared by methods other than those given in ISO 6713 (see 4.4.2.3), it will be necessary to modify the equations for the calculation of cadmium 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 contain at least the following information:

a) the type and identification of the product tested;

b) a reference to this International Standard (ISO 3856/4);

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), where appropriate [1];

d) the solvent or the solvent mixture used for the extraction, where appropriate [1];

e) the method of determination (AAS or polarographic) used;

f) the results of the test, each expressed as a percentage by mass of the product: either

— the "soluble" cadmium content of the pigment portion of the paint, the cadmium content of the liquid portion of the paint and the total "soluble" cadmium content of the liquid paint,

or

— the total "soluble" cadmium content of the paint in powder form;

g) any deviation, by agreement or otherwise, from the test procedure specified;

h) the date of the test.

1) Not required for paints in powder form (see clause 7 of ISO 6713).