International Standard ISO 3856/2

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Paints and varnishes — Determination of "soluble" metal content —
Part 2: Determination of antimony content — Flame atomic absorption spectrometric method and Rhodamine B spectrophotometric method

Peintures et vernis — Détermination de la teneur en métaux «solubles» — Partie 2: Détermination de la teneur en antimoine — Méthode par spectrométrie d'absorption atomique dans la flamme et méthode spectrophotométrique à la rhodamine B

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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 preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. 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 2: Determination of antimony content — Flame atomic absorption spectrometric method and Rhodamine B 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 antimony content of the test solutions prepared according to ISO 6713 or other suitable International Standards.

The methods are applicable to paints having "soluble" antimony 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 Rhodamine B 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 an antimony hollow-cathode or antimony discharge lamp, in the region of 217,6 nm (see also 3.5).

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, approximately 37 % (*m/m*) (ϱ approximately 1,18 g/ml).

3.2.2 Hydrochloric acid, $c(\mathrm{HCl}) = 1$ mol/l.

3.2.3 Acetylene, commercial grade, in a steel cylinder.

3.2.4 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.

3.2.5 Antimony, standard stock solution containing 1 g of Sb per litre.

Weigh, to the nearest 0,1 mg, 119,7 mg of dried antimony trioxide, dissolve in 40 ml of the hydrochloric acid (3.2.1) in a 100 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 Sb.

3.2.6 Antimony, standard solution containing 100 mg of Sb per litre.

Prepare this solution on the day of use.

Pipette 10 ml of the standard stock solution (3.2.5) into a 100 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (3.2.2) and mix well.

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

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 Flame atomic absorption spectrometer, suitable for measurements at a wavelength of 217,6 nm and fitted with a burner fed with acetylene and air.

3.3.2 Antimony hollow-cathode lamp or **antimony 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 five 100 ml one-mark volumetric flasks (3.3.4), introduce from the burette (3.3.3), respectively, the volumes of the standard antimony solution (3.2.6) shown in the following table, dilute each to the mark with the hydrochloric acid (3.2.2) and mix well.

Standard matching solution No.	Volume of the standard antimony solution (3.2.6)	Corresponding concentration of Sb in the standard matching solution
	ml	µg/ml
0 *	0	0
1	5	5
2	10	10
3	20	20
4	40	40

* Blank matching solution.

3.4.1.2 Spectrometric measurements

Install the antimony spectral source (3.3.2) in the spectrometer (3.3.1) and optimize the conditions for the determination of antimony. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 217,6 nm in order to obtain the maximum absorbance.

Adjust the flow of the acetylene (3.2.3) and of the air (3.2.4) 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 Sb 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

Mix thoroughly 9 parts by volume of each of the solutions obtained by the procedure described in sub-clause 8.2.3 of ISO 6713 with 1 part by volume of the hydrochloric acid (3.2.1).

3.4.2.2 Liquid portion of the paint

Mix thoroughly 9 parts by volume of each of the solutions obtained by the procedure described in sub-clause 9.3 of ISO 6713 with 1 part by volume of the hydrochloric acid (3.2.1).

3.4.2.3 Other test solutions

Use the test solutions obtained by other specified or agreed procedures. Take care that the acidity of the solutions is about 1 mol/l.

3.4.3 Determination

Measure first the absorbance of the hydrochloric acid (3.2.2) 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 antimony concentration, dilute the test solution appropriately (dilution factor F) with a known volume of the hydrochloric acid (3.2.2).

3.5 Interferences

Spectral interference occurs in the presence of lead, calcium or copper on the resonance line at 217,6 nm. In the presence of lead, use the antimony resonance line at 206,8 nm, or 231,1 nm. In the presence of calcium, measure the absorbance at 217,0 nm and subtract the result from the absorbance at 217,6 nm. In the presence of copper, use the antimony resonance line at 231,1 nm.

Use a deuterium background corrector to correct for background absorption. Alternatively, the solutions can be re-aspirated using a neighbouring non-absorbing line for the background correction (see the note).

NOTE — Some hollow-cathode lamps for antimony have a non-absorbing line at 216,9 nm.

3.6 Expression of results

3.6.1 Calculations

3.6.1.1 Pigment portion of the liquid paint

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

$$m_0 = \frac{a_1 - a_0}{10^6} \times V_1 \times \frac{10}{9} \times F_1$$

$$= (a_1 - a_0) \times V_1 \times F_1 \times \frac{10^{-5}}{9}$$

where

a_0 is the antimony 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 antimony 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" antimony 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" antimony content of the pigment portion of the paint, using the equation

$$c_{\mathrm{Sb}_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where

c_{Sb_1} is the "soluble" antimony 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 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.

3.6.1.2 Liquid portion of the paint

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

$$m_2 = \frac{b_1 - b_0}{10^6} \times V_2 \times \frac{10}{9} \times F_2$$

$$= (b_1 - b_0) \times V_2 \times F_2 \times \frac{10^{-5}}{9}$$

where

b_0 is the antimony 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 antimony 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 antimony 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 antimony content of the liquid portion of the paint, using the equation

$$c_{\mathrm{Sb}_2} = \frac{m_2}{m_3} \times 10^2$$

where

c_{Sb_2} is the antimony 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.

3.6.1.3 Liquid paint

Calculate the total "soluble" antimony content of the liquid paint as the sum of the results obtained according to 3.6.1.1 and 3.6.1.2, thus

$$c_{Sb_3} = c_{Sb_1} + c_{Sb_2}$$

where c_{Sb_3} is the total "soluble" antimony content of the paint, expressed as a percentage by mass.

3.6.1.4 Paint in powder form

The total "soluble" antimony content of the paint in powder form is obtained by appropriate modification of the calculations given in 3.6.1.1.

3.6.1.5 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 antimony content given in 3.6.1.1 and 3.6.1.2.

3.6.2 Precision

No precision data are currently available.

4 Rhodamine B spectrophotometric method

4.1 Principle

After oxidation, extraction of the antimony from strong hydrochloric acid solution with di-*iso*propyl ether. Formation of a red complex with Rhodamine B solution, and spectrophotometric measurement of the colour at a wavelength of about 553 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, approximately 37 % (*m*/*m*) (ϱ approximately 1,18 g/ml).

4.2.2 Nitric acid, approximately 65 % (*m*/*m*) (ϱ approximately 1,40 g/ml).

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

4.2.4 Di-*iso*propyl ether.

4.2.5 Rhodamine B solution.

Dissolve 150 mg of Rhodamine B (this is the trade name for tetraethylrhodamine) in 1 000 ml of hydrochloric acid, $c(\text{HCl}) = 0{,}8$ mol/l, and mix well.

4.2.6 Cerium(IV) sulfate.

4.2.7 Antimony, standard stock solution containing 200 mg of Sb per litre.

Weigh, to the nearest 0,1 mg, 239,4 mg of dried antimony trioxide, dissolve in 100 ml of the hydrochloric acid (4.2.1) 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 200 µg of Sb.

4.2.8 Antimony, standard solution containing 4 mg of Sb per litre.

Prepare this solution on the day of use.

Pipette 20 ml of the standard stock solution (4.2.7) into a 1 000 ml one-mark volumetric flask, add 50 ml of the hydrochloric acid (4.2.1), dilute to the mark with water and mix well.

1 ml of this standard solution contains 4 µg of Sb.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 Spectrophotometer, suitable for measurements at a wavelength of about 553 nm, fitted with cells of optical path length 10 or 20 nm.

4.3.2 Separating funnels, of capacity 100 ml, complying with the requirements of ISO 4800.

4.3.3 Pipettes, of capacity 20 ml, complying with the requirements of ISO 648.

4.3.4 Burette, of capacity 25 ml, complying with the requirements of ISO 385/1.

4.3.5 One-mark volumetric flasks, of capacity 50 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.

Into a series of five 100 ml beakers, introduce from the burette (4.3.4), respectively, the volumes of the standard antimony solutions (4.2.8) shown in the following table.

Standard colorimetric solution No.	Volume of the standard antimony solution (4.2.8)	Corresponding concentration of Sb in the standard colorimetric solution
	ml	µg/ml
0 *	0	0
1	5	0,4
2	10	0,8
3	15	1,2
4	20	1,6

* Compensation solution.

Treat the contents of each beaker as follows.

Add a few millilitres of the nitric acid (4.2.2) and 2 ml of the sulfuric acid (4.2.3) and evaporate almost to dryness. Add 20 ml of the hydrochloric acid (4.2.1) to the mixture and, to oxidize the antimony, about 2 mg of the cerium(IV) sulfate (4.2.6) or until the solution becomes slightly yellow due to the presence of excess cerium(IV) sulfate. Ensure that the temperature during the oxidation does not exceed 30 °C.

Allow to stand for several minutes, add 20 ml of the di-*iso*propyl ether (4.2.4) and mix carefully. Transfer the mixture, washing with 30 ml of water, into a 100 ml separating funnel A (4.3.2) and shake vigorously. Allow to stand for 5 min and transfer the lower aqueous phase into a second separating funnel. Add 7 ml of the di-*iso*propyl ether to the second funnel B, shake vigorously and reject the aqueous phase.

Add 20 ml of the Rhodamine B solution (4.2.5) to the separating funnel A, containing 20 ml of the di-*iso*propyl ether and shake the mixture carefully. After the phases have separated, transfer the aqueous Rhodamine B solution to the separating funnel B, containing 7 ml of the di-*iso*propyl ether and shake carefully. Allow the phases to separate and reject the Rhodamine B solution.

Collect both di-*iso*propyl ether extracts plus any washings in a 50 ml one-mark volumetric flask (4.3.5), dilute to the mark with the di-*iso*propyl ether, and mix well.

4.4.1.2 Spectrophotometric measurements

Measure the absorbances of the standard colorimetric solutions (4.4.1.1) with the spectrophotometer (4.3.1) at the wavelength of maximum absorption (about 553 nm) against di-*iso*propyl ether (4.2.4) in the reference cell. Before each measurement, rinse the cell with the standard colorimetric solution. Deduct the absorbance of the compensation solution from those of the other standard colorimetric solutions.

4.4.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Sb 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.

NOTE — It is essential that the oxidation be carried out in a solution containing a high concentration of hydrochloric acid. Any dilution of the hydrochloric acid before addition of di-*iso*propyl ether leads to lower results. During extraction, the hydrochloric acid concentration of the aqueous solution should be about 5 mol/l.

The di-*iso*propyl ether solutions of the complex are only stable for a limited time and their absorbances should be measured within 3 h.

4.4.2 Test solutions

4.4.2.1 Pigment portion of the liquid paint

Use the solutions obtained by the procedure described in sub-clause 8.2.3 of ISO 6713.

4.4.2.2 Liquid portion of the paint

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

4.4.2.3 Other test solutions

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

4.4.3 Determination

Carry out the colour development, in a series of three 100 ml beakers, by the procedure described in 4.4.1.1, using volumes of the test solutions (4.4.2) such that their absorbances will be within the calibration range. Measure each absorbance by the procedure described in 4.4.1.2.

NOTE — If iron is present in the hydrochloric acid extract, a previous separation by extraction of antimony(III) iodide in sulfuric acid with toluene may be necessary.

4.5 Expression of results

4.5.1 Calculations

4.5.1.1 Pigment portion of the liquid paint

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

$$m_0 = \frac{(a_1 - a_0)}{10^6} \times \frac{V_1}{V_3} \times 50$$

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

where

a_0, a_1, m_0 and V_1 are as defined in 3.6.1.1;

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

Calculate the "soluble" antimony content of the pigment portion of the paint, using the equation

$$c_{\mathrm{Sb}_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where c_{Sb_1}, m_1 and P are as defined in 3.6.1.1.

4.5.1.2 Liquid portion of the paint

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

$$m_2 = \frac{b_1 - b_0}{10^6} \times \frac{V_2}{V_4} \times 50$$

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

where

b_0, b_1, m_2 and V_2 are as defined in 3.6.1.2;

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

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

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

where c_{Sb_2} and m_3 are as defined in 3.6.1.2.

4.5.1.3 Liquid paint

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

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

where c_{Sb_3} is as defined in 3.6.1.3.

4.5.1.4 Paint in powder form

The total "soluble" antimony 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 antimony 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 3856/2);

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 Rhodamine B spectrophotometric) used;

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

- the "soluble" antimony content of the pigment portion of the paint, the antimony content of the liquid portion of the paint and the total "soluble" antimony content of the liquid paint, or
- the total "soluble" antimony 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.

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