International Standard 3856/2

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Paints and varnishes — Determination of "soluble" metal content — Part 2 : Determination of antimony content — Flame atomic absorption spectroscopic 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 spectroscopie d'absorption atomique dans la flamme et méthode spectrophotométrique à la rhodamine B

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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 :

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Paints and varnishes — Determination of "soluble" metal content —
Part 2 : Determination of antimony content — Flame atomic absorption spectroscopic method and Rhodamine B 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 antimony 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 photometric method is agreed, the Rhodamine B spectrophotometric 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 an antimony hollow-cathode or antimony discharge 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, approximately 37 % (m/m) solution, ϱ approximately 1,18 g/ml.

3.2.2 Hydrochloric acid, 1 mol/l solution.

3.2.3 Acetylene, in a steel cylinder.

3.2.4 Compressed air.

3.2.5 Antimony, standard solution corresponding to 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 solution (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 solution contains 1 mg of Sb.

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

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

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

Prepare this solution on the day of use.

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, 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/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 antimony solution (3.2.6) shown in the following table, dilute each to the mark with the hydrochloric acid solution (3.2.2) and mix well.

Prepare these solutions on the day of use.

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

* Blank test on reagents for calibration graph.

3.4.1.2 Spectroscopic measurement

Install the antimony hollow-cathode or discharge 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 217,6 nm (see also 3.5) in order to obtain the maximum absorbance. Adjust the pressures of the acetylene (3.2.3) and of the air (3.2.4) 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 Sb 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

Mix thoroughly 9 parts by volume of the solution obtained by the procedure specified in sub-clause 7.2.1 of ISO 6713 with 1 part by volume of hydrochloric acid solution (3.2.1).

3.4.2.2 Liquid portion of the paint

Mix thoroughly 9 parts by volume of the solution obtained by the procedure specified in clause 8 of ISO 6713 with 1 part by volume of hydrochloric acid solution (3.2.1).

3.4.2.3 Other test solutions

Use the test solution 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 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 (3.2.2), 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 antimony concentration, dilute the test solution appropriately with a known volume of the hydrochloric acid solution (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 Pigments and extenders

The mass of "soluble" antimony in the hydrochloric acid extract, obtained by the method specified in sub-clause 7.2.1 of ISO 6713, is given by the equation

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

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

where

a_0 is the antimony concentration, in micrograms per millilitre, of the blank test solution prepared by the method specified in sub-clause 7.3 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 sub-clause 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 solution plus ethanol used for the extraction specified in sub-clause 7.2.1 of ISO 6713 (assumed to be 77 ml).

The "soluble" antimony content of the pigment and extender portion of the paint is given by 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 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.

3.6.1.2 Liquid portion of the paint

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

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

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

where

b_0 is the antimony concentration, in micrograms per millilitre, of the blank test solution prepared by the method specified 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 sub-clause 3.4.3;

m_2 is the mass, in grams, of antimony 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 antimony content of the liquid portion of the paint is given by 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 specified in sub-clause 6.4 of ISO 6713.

3.6.1.3 Paint

The total "soluble" antimony content of the paint is given by the sum of the results obtained according to 3.6.1.1 and 3.6.1.2, thus

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

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

3.6.1.4 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 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 distilled water or water of equivalent purity.

4.2.1 Hydrochloric acid, approximately 37 % (*m*/*m*) solution, ϱ approximately 1,18 g/ml.

4.2.2 Nitric acid, approximately 65 % (*m*/*m*) solution, ϱ approximately 1,42 g/ml.

4.2.3 Sulphuric acid, approximately 98 % (*m*/*m*) solution, 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 0,8 mol/l hydrochloric acid solution and mix well.

4.2.6 Cerium(IV) sulphate.

4.2.7 Antimony, standard solution corresponding to 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 solution (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 solution contains 200 µg of Sb.

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

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

Prepare this solution on the day of use.

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 mm.

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/R 385.

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 for spectrophotometric measurements in cells of optical path length 10 or 20 mm

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

Standard colorimetric solution No.	Standard antimony solution (4.2.8)	Corresponding concentration of Sb in 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 solution (4.2.2) and 2 ml of the sulphuric acid solution (4.2.3) and evaporate almost to dryness. Add 20 ml of the hydrochloric acid solution (4.2.1) to the mixture and, to oxidize the antimony, about 2 mg of the cerium(IV) sulphate (4.2.6). The solution should be slightly yellow due to the presence of excess cerium(IV) sulphate. The temperature during the oxidation shall 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 (4.3.2) and shake vigorously. Allow to stand for 5 min, transfer the lower aqueous phase into a second 100 ml separating funnel, add 7 ml of the di-*iso*propyl ether, shake vigorously and reject the aqueous phase.

Add 20 ml of the Rhodamine B solution (4.2.5) to the separating funnel 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 containing 7 ml of the di-*iso*propyl ether and shake carefully. Separate and reject the Rhodamine B solution.

Collect both di-*iso*propyl ether extracts plus 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.

Prepare these solutions on the day of use.

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 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 of the 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 absorbances 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 and extenders

Use the solution obtained by the procedure specified in sub-clause 7.2.1 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 test solution 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 specified 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 the absorbance by the procedure specified 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 sulphuric acid solution with toluene may be necessary.

4.5 Expression of results

4.5.1 Calculations

4.5.1.1 Pigments and extenders

The mass of "soluble" antimony in the hydrochloric acid extract, obtained by the method specified in sub-clause 7.2.1 of ISO 6713, is given by the equation

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

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

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 solution plus ethanol taken for the test.

The "soluble" antimony content of the pigment and extender portion of the paint is given by 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_0, m_1 and P are as defined in 3.6.1.1.

4.5.1.2 Liquid portion of the paint

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

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

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

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.

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

$$c_{Sb_2} = \frac{m_2}{m_3} \times 10^2$$

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

4.5.1.3 Paint

The total "soluble" antimony 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

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

where c_{Sb_3} is as defined in 3.6.1.3.

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 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 include at least the following information :

a) the type and identification of the product tested;

b) a reference to this International Standard (ISO 3856/2) or to a corresponding national standard;

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 spectrophotometric) used;

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

g) the results of the tests, each expressed as a percentage by mass of the product, i.e. the "soluble" antimony content of the pigment and extender, the antimony content of the liquid portion of the paint and the total "soluble" antimony content of the paint;

h) the date of the test.