

---

International Standard



3856/2

---

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

---

**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*

First edition — 1980-10-01

STANDARDSISO.COM : Click to view the full PDF of ISO 3856-2:1980

---

UDC 667.6 : 543.422 : 546.86

Ref. No. ISO 3856/2-1980 (E)

**Descriptors** : paints, varnishes, printing inks, chemical analysis, determination of content, soluble matter, metals, antimony, atomic absorption spectroscopic analysis.

## 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 3856/2 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	Iran	Poland
Austria	Ireland	Romania
Brazil	Israel	South Africa, Rep. of
Bulgaria	Italy	Sweden
Egypt, Arab Rep. of	Kenya	Switzerland
France	Korea, Rep. of	Turkey
Germany, F.R.	Mexico	United Kingdom
India	Norway	USSR

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

Canada

# 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.<sup>1)</sup>

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*.<sup>1)</sup>

### 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,  $\rho$  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.

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, re-determine 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

$$c_{Sb_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2}$$

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

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

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

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

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

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

**3.6.1.4 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-isopropyl 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,  $\rho$  approximately 1,18 g/ml.

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

**4.2.3 Sulphuric acid**, approximately 98 % (m/m) solution,  $\rho$  approximately 1,84 g/ml.

**4.2.4 Di-isopropyl 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  $\mu$ g 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  $\mu$ g 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	$\mu$ g/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