



DANSK  
STANDARDISERINGSRÅD

Malinger og lakker. Bestemmelse af »opløseligt« metalindhold. Bestemmelse af kviksølvindhold i pigmentdelen af malinger og i væskedelen af vandfortyndbare malinger. Flammeløs atomabsorptionsspektroskopisk metode

Dansk Standard

DS/ISO 3856/7

1. udg. Januar 1986  
UDK 667.6:543.422:  
546.49

*Paints and varnishes — Determination of »soluble« metal content  
Part 7: Determination of mercury content of the pigment portion of the  
paint and of the liquid portion of water-dilutable paints — Flameless  
atomic absorption spectrometric method*

Side 1 (8)

Denne standard er identisk (IDT) med International Standard ISO 3856/7, 1. udgave 1984.

*This standard is identical (IDT) with International Standard ISO 3856/7, 1st edition 1984.*

## 0 Introduction

ISO 3696, *Water for laboratory use — Specifications.*<sup>2)</sup>

This International Standard is a part of ISO 3856, *Paints and varnishes — Determination of "soluble" metal content.*

ISO 6713, *Paints and varnishes — Preparation of acid extracts from paints in liquid or powder form.*

## 1 Scope and field of application

This part of ISO 3856 describes a flameless atomic absorption spectrometric method for the determination of the mercury content of the test solutions, prepared according to ISO 6713 or other suitable International Standards.

The method is applicable to paints having "soluble" mercury contents in the range of about 0,005 to 0,05 % (*m/m*), but the part of this method covering the examination of the liquid portion of the paint is restricted to water-dilutable paints.

**CAUTION** — The procedures described in this part of ISO 3856 are intended to be carried out by qualified chemists or by other suitably trained and/or supervised personnel. The substances and procedures used in this method may be injurious to health if adequate precautions are not taken. Attention is drawn in the text (see 4.6 and 4.7) to certain specific hazards. This part of ISO 3856 refers only to its technical suitability and does not absolve the user from statutory obligations relating to health and safety.

## 2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*<sup>1)</sup>

ISO 648, *Laboratory glassware — One-mark pipettes.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

## 3 Principle

Oxidation of the mercury compounds contained in the test solution obtained from the pigment portion of the paint or combustion with oxygen in an enclosed system of the evaporation residue of the test solution obtained from the liquid portion of water-dilutable paints.

Reduction of the mercury(II) compounds contained in the resulting solutions to elementary mercury. Entrainment of the mercury in a current of gas at ambient temperature and determination of the mercury, as the monoatomic vapour, by cold vapour (flameless) atomic absorption spectrometry at a wavelength in the region of 253,7 nm.

## 4 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and water of at least grade 3 purity according to ISO 3696.

**4.1 Oxygen**, commercial grade, in a steel cylinder.

**4.2 Tin(II) chloride dihydrate**, 100 g/l solution.

Dissolve 25 g of tin(II) chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 50 ml of 35 % (*m/m*) ( $\rho$  approximately 1,18 g/ml) hydrochloric acid and dilute to 250 ml with water. Add a few granules of metallic tin and heat until any precipitate disappears. Ensure that a few granules of bright tin are present to stabilize the solution and, before use, that there is no precipitate.

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

2) At present at the stage of draft.



**4.3 Sulfuric acid, 5 % (m/m).****4.4 Nitric acid, approximately 65 % (m/m) ( $\rho$  approximately 1,40 g/ml).****4.5 Potassium permanganate, 60 g/l solution.**

Dissolve 60 g of potassium permanganate ( $\text{KMnO}_4$ ) in water and dilute to 1 litre.

**4.6 Hydroxylammonium chloride, 20 % (m/m) solution.**

**WARNING** — Hydroxylammonium chloride is toxic, corrosive and an irritant. Avoid contact with eyes and skin.

Dissolve 20 g of hydroxylammonium chloride ( $\text{NH}_2\text{OHCl}$ ) in about 75 ml of water and dilute to 100 ml.

**4.7 Mercury, standard stock solution containing 100 mg of Hg per litre.**

**WARNING** — Mercury, particularly in its vapour form, and its solutions are toxic. Avoid breathing mercury vapour. Avoid contact of mercury or its solutions with eyes and skin. Carry out all procedures in a well-ventilated fume cupboard.

Either

- a) transfer the contents of an ampoule of a standard mercury solution containing exactly 0,1 g of Hg into a 1 000 ml one-mark volumetric flask, dilute to the mark with the 5 % (m/m) sulfuric acid (4.3) and mix well;

or

- b) weigh, to the nearest 0,1 mg, 0,135 4 g of mercury(II) chloride, dissolve in the sulfuric acid (4.3) in a 1 000 ml one-mark volumetric flask, dilute to the mark with the same sulfuric acid and mix well.

1 ml of this standard stock solution contains 0,1 mg of Hg.

**4.8 Mercury, standard solution containing 1 mg of Hg per litre.**

Prepare this solution on the day of use.

Pipette 10 ml of the standard stock solution (4.7) into a 1 000 ml one-mark volumetric flask, dilute to the mark with the sulfuric acid (4.3) and mix well.

1 ml of this standard solution contains 1  $\mu\text{g}$  of Hg.

**5 Apparatus**

Ordinary laboratory apparatus and

**5.1 Atomic absorption spectrometer**, suitable for measurements at a wavelength of 253,7 nm and capable of operating with the measuring cell specified in 5.2.

NOTE — If special commercial mercury analyzers using the cold vapour AAS principle are used (see note to 6.1.2.1), appropriate amendment of the procedure described in 6.1.2 and 6.3.2 may be necessary and this should be recorded in the test report.

**5.2 Measuring cell**, with windows (for example of quartz) transparent to ultraviolet radiation (in the region of 253,7 nm), the optical path length of which should be appropriate to the spectrometer being used, but not less than 100 mm.

**5.3 Mercury hollow-cathode lamp or mercury discharge lamp.**

**5.4 Potentiometric chart recorder.**

NOTE — A suitable peak measuring device such as an electronic integrator may be used as an alternative.

**5.5 Combustion flask or separating funnel**, of capacity 500 ml, with a ground-glass joint.

**5.6 Test portion holder** (platinum gauze combustion basket) and **firing adapter**, suitable for fitting to the combustion flask (5.5) (see figure 1).

**5.7 Spark generator.**

NOTE — A high-frequency vacuum tester has been found to be satisfactory.

**5.8 Flowmeter**, fitted with a stainless steel needle valve and capable of measuring flow rates within the range 0,4 to 3 l/min.

**5.9 Pump**, diaphragm type, capable of giving controlled air flow rates of 0,4 to 3 l/min, or **cylinder of compressed air or nitrogen** equipped with a suitable pressure regulating valve.

**5.10 Reaction vessel**, comprising a test tube, of capacity 25 ml, with a ground-glass joint neck to fit an interchangeable head and a four-way stopcock (see figure 2).

**5.11 Equipment**, to prevent any condensation of water vapour in the measuring cell. Any appropriate system may be used for this purpose (for example an infra-red lamp, a black electrical heating element, or a rod heater).

**5.12 Flexible acid-resistant tubing** (for example silicone rubber tubing), suitable for connecting the apparatus (see figure 2).

**5.13 Capsules**, of hardened gelatine, pharmaceutical grade.

**5.14 Rotary evaporator**, water cooled, capable of operation under vacuum with a rotation rate of 150 r/min.

**5.15 Water-bath**, capable of being maintained at  $45 \pm 5$  °C.

**5.16 Burettes**, of capacity 10 ml and 25 ml, complying with the requirements of ISO 385/1.

**5.17 One-mark volumetric flasks**, of capacity 25 ml, 100 ml and 500 ml, complying with the requirements of ISO 1042.

**5.18 Pipettes**, of capacity 1 ml, 5 ml and 25 ml, complying with the requirements of ISO 648.

**5.19 Balance**, capable of weighing to 0,1 mg.

## 6 Procedure

### 6.1 Preparation of the calibration graph

#### 6.1.1 Preparation of the standard matching solutions

Prepare these solutions on the day of use.

Into a series of six 25 ml one-mark volumetric flasks (5.17), introduce from the 10 ml burette (5.16), respectively, the volumes of the standard mercury solution (4.8) shown in the following table, dilute each to the mark with the sulfuric acid (4.3) and mix well.

Standard matching solution No.	Volume of the standard mercury solution (4.8)	Corresponding concentration of Hg in the standard matching solution
	ml	µg/ml
0*	0	0
1	1	0,04
2	2	0,08
3	3	0,12
4	4	0,16
5	5	0,20

\* Blank matching solution.

#### 6.1.2 Spectrometric measurement

**6.1.2.1** Install the measuring cell (5.2) and the mercury spectral source (5.3) in the spectrometer (5.1) and optimize the conditions for the determination of mercury. Adjust the instrument in accordance with the manufacturer's instructions and adjust the monochromator to the region of 253,7 nm in order to obtain the maximum absorbance. Connect the flowmeter (5.8), pump (5.9), reaction vessel (5.10) and measuring cell (5.2) with the minimum lengths of flexible tubing (5.12) as shown in figure 2.

NOTE — A closed-circuit measuring system may be used in which the mercury is recirculated by means of a pump. This will be particularly effective when the release of mercury vapour is delayed by interfering substances, e.g. bromide ions.

**6.1.2.2** Switch on the pump and move the four-way stopcock to the by-pass position. Adjust the needle valve or open the gas regulating valve to give a suitable flow rate (for example

1 l/min). Set the potentiometric chart recorder (5.4) to the appropriate range. Adjust the zero of the recorder to a suitable position on the chart and check for baseline drift and noise level (see 6.1.2.4).

**6.1.2.3** Disconnect the reaction vessel and, using a pipette (5.18), place 5 ml of the standard matching solution No. 5 into the vessel. Add by means of a pipette (5.18) 1 ml of the tin(II) chloride solution (4.2), mix well and immediately reconnect the reaction vessel. Reverse the four-way stopcock to allow the liberated mercury vapour to be swept through the measuring cell.

**6.1.2.4** A peak will be indicated on the recorder chart and, by means of the potentiometer and flow range controls, adjust the height of the peak on the chart to about one-half the full-scale reading. Ensure that a sharp peak is obtained. Repeat if a further check of the adjustment is required.

Return the stopcock to the by-pass position and repeat the procedure using 5 ml aliquot portions of the remaining standard matching solutions.

NOTE — It may be necessary to repeat the initial test several times using the standard matching solution No. 5 in order to optimize the characteristics of the system.

#### 6.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Hg contained in 1 ml of the standard matching solutions as abscissae and the corresponding peak heights or, more precisely, the peak areas (for example, the products of the peak height and the peak width at half the peak height), reduced by the value for the blank matching solution, as ordinates.

Over this range the curve should deviate only slightly from linearity.

NOTE — Contamination of any portion of the apparatus with aromatic solvents may give false high results owing to absorption in the region of 254 nm.

## 6.2 Test solutions

### 6.2.1 Pigment portion of the liquid paint and paint in powder form

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

Carry out the following oxidation procedure in duplicate.

Pipette a 5 ml aliquot portion of each test solution into individual 100 ml one-mark volumetric flasks (5.17). Add to each flask, 50 ml of the sulfuric acid (4.3), followed by 10 ml of the potassium permanganate solution (4.5). Allow to stand for a minimum of 2 h or preferably overnight to ensure that the mercury is present as Hg(II). After this period, add 2 ml of the hydroxylammonium chloride solution (4.6) and mix gently to obtain a clear, almost colourless solution. Dilute to the mark with the sulfuric acid (4.3) and mix well.