International Standard 3856/5

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

Paints and varnishes — Determination of "soluble" metal content — Part 5: Determination of hexavalent chromium content of the pigment portion of the liquid paint or the paint in powder form — Diphenylcarbazide spectrophotometric method

Peintures et vernis — Détermination de la teneur en métaux «solubles» — Partie 5: Détermination du chrome hexavalent contenu dans le pigment de la peinture liquide ou de la peinture en poudre — Méthode spectrophotométrique à la diphénylcarbazide

Second edition — 1984-11-01

UDC 667.6 : 543.42 : 546.766 **Ref. No. ISO 3856/5-1984 (E)**

Descriptors: paints, varnishes, printing inks, pigments, chemical analysis, determination of content, chromium, spectrophotometry, diphenylcarbazide.

Price based on 3 pages

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.

International Standard ISO 3856/5 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

ISO 3856/5 was first published in 1980. This second edition cancels and replaces the first edition, of which it constitutes a thorough revision.

Printed in Switzerland

Paints and varnishes — Determination of "soluble" metal content — Part 5: Determination of hexavalent chromium content of the pigment portion of the liquid paint or the paint in powder form — Diphenylcarbazide 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 a diphenylcarbazide spectrophotometric method for the determination of the "soluble" hexavalent chromium content of the hydrochloric acid extract of the pigment portion of the liquid paint or of the paint in powder form, prepared in accordance with sub-clause 8.2.3 of ISO 6713 or other suitable International Standards.

The method is applicable to paints having hexavalent chromium contents in the range of about 0,05 to 5 % (*m/m*).

Other methods can be used by agreement between the interested parties, provided that the methods are specific for hexavalent chromium but this spectrophotometric method is the referee method in cases of dispute.

2 References

ISO 385/1, *Laboratory glassware — Burettes — Part 1: General requirements.*[1]

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 Principle

Formation of a coloured complex from hexavalent chromium and diphenylcarbazide solution. After addition of orthophosphoric acid and sulfuric acid, spectrophotometric measurement of the colour at a wavelength in the region of 540 nm.

4 Reagents

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

4.1 Diphenylcarbazide, solution.

Dissolve 0,25 g diphenylcarbazide in a mixture of 50 ml of acetone and 50 ml of water.

4.2 Sodium hydroxide, $c(NaOH) = 2$ mol/l solution.

4.3 Sulfuric acid, $c(H_2SO_4) = 1$ mol/l.

4.4 Orthophosphoric acid, approximately 85 % (*m/m*) (ϱ approximately 1,69 g/ml).

4.5 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 6.2.)

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

2) At present at the stage of draft.

4.6 Hexavalent chromium, standard stock solution containing 100 mg of Cr(VI) per litre.

Weigh, to the nearest 0,1 mg, 282,9 mg of dry potassium dichromate, dissolve in water 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 100 µg of Cr(VI).

4.7 Hexavalent chromium, standard solution containing 1 mg of Cr(VI) per litre.

Prepare this solution on the day of use.

Pipette 10 ml of the standard stock solution (4.6) into a 1 000 ml one-mark volumetric flask, dilute to the mark with the hydrochloric acid (4.5) and mix well.

1 ml of this standard solution contains 1 µg of Cr(VI).

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrophotometer, suitable for measurements at a wavelength of about 540 nm, fitted with cells of optical path length 10 or 20 mm.

5.2 pH-meter, with glass electrode and reference electrode.

5.3 Burette, of capacity 50 ml, complying with the requirements of ISO 385/1.

5.4 One-mark volumetric flasks, of capacity 50 ml, complying with the requirements of ISO 1042.

6 Procedure

6.1 Preparation of the calibration graph

6.1.1 Preparation of standard colorimetric solutions

Prepare these solutions on the day of use.

Into a series of five 50 ml beakers, introduce from the burette (5.3), respectively, the volumes of the standard hexavalent chromium solution (4.7) shown in the following table.

Standard colorimetric solution No.	Volume of the standard hexavalent chromium solution (4.7)	Corresponding concentration of Cr(VI) in the standard colorimetric solution
	ml	µg/ml
0 *	0	0
1	5	0,1
2	10	0,2
3	15	0,3
4	20	0,4

* Compensation solution.

Treat the contents of each beaker as follows:

Add 5 ml of the sodium hydroxide solution (4.2). Using the pH-meter (5.2), adjust the pH value of the solution to 7,0 by the addition of the sulfuric acid (4.3). Add 2 ml of the diphenylcarbazide solution (4.1) and 1 to 2 ml of the orthophosphoric acid (4.4), together with 5 ml of the sulfuric acid (4.3). Transfer to a 50 ml one-mark volumetric flask (5.4), dilute to the mark with water and mix well.

6.1.2 Spectrophotometric measurements

Immediately measure the absorbances of the standard colorimetric solutions (6.1.1) with the spectrophotometer (5.1) at the wavelength of maximum absorption (about 540 nm) against water 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.

6.1.3 Calibration graph

Plot a graph having the masses, in micrograms, of Cr(VI) 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.

6.2 Test solutions

Use the solutions obtained by the procedure described in subclause 8.2.3 of ISO 6713 or other specified or agreed procedures.

6.3 Determination

Introduce from the burette (5.3), into a 50 ml beaker, a volume of each of the test solutions (6.2) such that its absorbance lies on the calibration graph. Treat the solution as described in 6.1.1. Measure the absorbance as described in 6.1.2.

7 Expression of results

7.1 Calculations

Calculate the mass of "soluble" hexavalent chromium 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 is the hexavalent chromium 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 hexavalent chromium concentration, in micrograms per millilitre, of the test solution obtained from the calibration graph;

m_0 is the mass, in grams, of "soluble" hexavalent chromium in the hydrochloric acid extract;

V_1 is the volume, in millilitres, of the hydrochloric acid plus ethanol taken for the extraction described in sub-clause 8.2.3 of ISO 6713 (assumed to be 77 ml);

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

Calculate the "soluble" hexavalent chromium content of the pigment portion of the paint using the equation

$$c_{Cr_1} = m_0 \times \frac{10^2}{m_1} \times \frac{P}{10^2} = \frac{m_0 \times P}{m_1}$$

where

c_{Cr_1} is the "soluble" hexavalent chromium 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.

NOTES

1 The total "soluble" chromium content of the liquid paint, consisting of the "soluble" hexavalent chromium content of the pigment portion plus the total chromium content of the liquid portion of the paint and expressed as a percentage by mass of the paint, is given by the sum of the results obtained according to ISO 3856/6 and this part of ISO 3856.

2 The total "soluble" hexavalent chromium content of the paint in powder form is obtained by appropriate modification of the calculations given in 7.1.

If the test solutions were prepared by methods other than that given in ISO 6713 (see 6.2), it will be necessary to modify the equations for the calculation of hexavalent chromium content given above.

7.2 Precision

No precision data are currently available.

8 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 3856/5);

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

— the "soluble" hexavalent chromium content in the pigment portion of the paint, or

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

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

g) the date of the test.

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