

WIDE CIRCULATION DOCUMENT
LAST DATE OF COMMENTS_08 01 2021

IS 101 (part 8/sec 5): xxxx
Doc No. CHD/20/16648

भारतीय मानक मसौदा

रोगनो, वार्निशों और संबंध उत्पादों के नमूने लेने और
परिक्षण की पद्धतियाँ
भाग 8 वर्णकों और अन्य ठोसों के परीक्षण
अनुभाग 5 सीसा प्रतिबंध परीक्षण
(चौथा पुनरीक्षण)

Draft Indian Standard

Methods of sampling and test for paints varnishes and related products

Part 8 Tests for Pigments and other Solids
Section 5 Lead Restriction Test
(Fourth Revision)

ICS 19.120

© BIS 2020

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

December 2020

Price Group

Paints, Varnishes and Related Products Sectional Committee, CHD 20

FOREWORD

(Formal clauses will be added later)

This standard (Part 8/Sec5) is one of a series dealing with methods of sampling and test for paints, varnishes and related products. In the third revision three test methods were prescribed for determination of lead in lead restricted paints. Further, in the

Fourth revision, Atomic Absorption Spectroscopy method has been incorporated. Any of the four methods can be used, but in case of dispute, 'Electrolysis Method' being the referee method shall be followed. This standard supersedes clauses 28 and 29 of IS 101:1964 Method of test for ready mixed paints and enamels (second revision).

In reporting the result of a test or analysis made in accordance with this standard, If the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (revised)'.

Draft Indian Standard

**METHODS OF SAMPLING AND TEST FOR
PAINTS, VARNISHES AND RELATED
PRODUCTS**

**PART 8 TESTS FOR PIGMENTS AND OTHER SOLIDS
Section 5 Lead Restriction Test**

(Fourth Revision)

1 SCOPE

This standard (Part 8/Sec 5) prescribes methods of test for lead restriction and freedom from lead in paint and allied products. For lead restriction test any one of the following three methods may be used:

- 1.1** Electrolysis method;
- 1.2** Molybdate method;
- 1.3** Sulphide method;
- 1.4** Atomic Absorption Spectroscopy method

'1.1 Electrolysis method shall be used as a referee method in case of any dispute.'

2 LEAD RESTRICTION

2.1 Electrolysis Method

2.1.1 Procedure

Transfer about 5 g of well mixed paint to a tared evaporating dish and dry at 105°C to constant mass. Place the exact mass of the dried sample in a muffle furnace and ash it for 20 min, at 315°C, 40 min at 425°C and 1 h at 540°C. Cool in a desiccator. Extract the ash in a 250 ml beaker with 30 ml cone nitric acid and 80-ml. water and heat to boil. Filter into a 400-ml beaker using fine texture paper to prevent manganese dioxide from passing into the filtrate. Wash with water.

Dilute the filtrate to approximately 300 ml, add 20 ml of 20 percent solution of ammonium nitrate and 10 ml of 0.1 percent copper sulphate solution.

Heat nearly to boiling and electrolyse using platinum gauze anode that has been weighed previously.

Electrolyse for 15 min each at 1A, 2A and then at 3A current. Rinse the electrode

three times in water with the current still on. Then remove the anodes, rinse in alcohol, dry for 15 min in an oven at $105 \pm 5^\circ\text{C}$. Cool and weigh.

NOTE —The electrodes should be cleaned after each determination. This is best done by placing them in nitric acid solution (1 :4) that contains a few ml of concentrated hydrogen peroxide (H_2O_2 , 30 percent), rinsed with water and dried for next use.

2.1.2 Calculation

Lead, percent by mass

$$\text{on non-volatile vehicle} = \frac{M \times 0.86623 \times 100}{W}$$

where

M = mass, in g, of lead oxide PbO_a , and

W = mass of non-volatile vehicle taken.

2.2 Molybdate Method

2.2.1 Outline of the Method

Paint is digested with concentrated sulphuric acid and nitric acid in order to convert lead to lead sulphate followed by extraction with ammonium acetate. Finally lead is precipitated as lead molybdate and weighed as lead molybdate.

2.2.2 Procedure

Transfer about 5 g of well mixed paint to a 400-ml beaker and dry at 105°C . Weigh accurately, add 20 ml of concentrated nitric acid and 15 ml of concentrated sulphuric acid and digest in order to remove all organic material and change lead to lead sulphate. Remove traces of nitric acid by repeated fuming with sulphuric acid. Cool, add 50 ml of water, heat to dissolve the salts and add 50 ml of ethyl alcohol and set aside for several hours. Filter through a paper pulp pad and wash with dilute sulphuric acid (1 : 20 v/v) containing 10 percent of ethyl alcohol. Dissolve the lead sulphate in three 10-ml portions of hot 20 percent ammonium acetate solution, followed by several washings with hot water. Treat the combined filtrate and washings with 2 ml of glacial acetic acid, heat to boil, add 10 ml of 5 percent aqueous ammonium paramolybdate solution and boil for a few minutes until the lead molybdate precipitate has coagulated.

Filter through a porcelain filtering crucible and wash with ammoniacal 2 percent ammonium nitrate solution. Heat to dull redness at $600 - 650^\circ\text{C}$ to constant mass.

2.2.3 Calculation

Lead content,

Percent by mass on

$$\text{non-volatile matter} = \frac{0.56436 \times W}{S} \times 100$$

where

W = mass of lead molybdate, and
 S = mass of dry sample taken for test.

2.3 Sulphide Method

2.3.1 Outline of the method

Determination of lead in lead restricted paints is carried out by precipitating the lead as sulphide from the separated pigment, which is finally oxidized to lead sulphate.

2.3.2 Procedure

Shake about one gram of the ground pigment obtained after treatment of paints as prescribed in IS 101 (Part 8/Sec 2), accurately weighed, continuously for one hour at room temperature with 1 000 times its weight of an aqueous solution of hydrochloric acid containing 0.25 percent by mass of hydrogen chloride. Allow the mixture to stand for one hour and then filter. Precipitate the lead salt contained in the clear filtrate as lead sulphide, filter, heat the lead sulphide in air to convert it into lead sulphate, weigh, calculate as lead monoxide (PbO) and express the result as percentage on the dry weight of the material taken for test.

2.4.3 Calculation

$$\text{Lead (as PbO)} = \frac{M_1}{M} \times 100$$

Where

M_1 = mass, in g, of the precipitate; and
 M = mass, in g, of the sample taken for the test.

2.4 Atomic Absorption Spectroscopy

2.4.1 Scope

This method covers the determination of Lead content in pigmented coating, it is also applicable for varnish and lacquer. This method is not applicable for determination of lead in sample containing antimony pigment as low recovery is obtained, it is not applicable if lead is present in sample to be analyzed in the form of organic lead compound.

2.4.2 Outline of the method

The liquid coating or dried film is prepared by dry ashing. The content of lead of an acid extract of ash is determined by Atomic absorption spectrophotometer.

2.4.3 Apparatus

2.4.3.1 Atomic Absorption Spectrophotometer

2.4.3.2 Muffle furnace capable of maintaining temp $500 \pm 10^\circ\text{C}$

2.4.3.3 Hot Plate capable of maintaining temp range 70 to 250°C

2.4.3.4 Glass Beaker 150ml, 250ml capacity

2.4.3.5 Porcelain Crucible 50 ml or porcelain dish 100 ml capacity

2.4.3.6 Pipette 1, 2, 5, 10 ml capacity.

2.4.3.7 Dropping bottle

2.4.4 *Reagent*

2.4.4.1 Nitric Acid (Specific Gravity 1.42)

2.4.4.2 Ammonium Acetate $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (50% wt / vol)

2.4.4.3 Lead Standard Stock Solution

2.4.5 *Procedure*

Mix the liquid coating, mix it until it is homogeneous. Prepare two replicate specimen by weighing by difference from dropping bottle approximately 2 to 3gms mixed liquid paint. Place the crucible containing liquid coating on hot plate and slowly increase the temp till it is dried. Gradually increase the temperature of hot plate till the material chars. After charring completely it is placed in a preheated furnace and ash at 475 to 500°C. Care should be taken

So that the temperature does not exceed 500°C otherwise there may be a loss by volatilization.

When the ashing appears to be complete remove the crucible from the muffle furnace allow to cool to room temp. Break up the ash in to fine particles with glass rod add 10 ml of dil Nitric Acid (1+1) taking care to avoid spattering in case the ash reacts vigorously. Heat till the volume reduces to 2 to 3ml, add additional 10ml of dil HNO_3 (1+1) continue heating.

Filter the solution through filter paper into 50ml volumetric flask. Wash the container three times with 2.5ml of hot ammonium acetate solution each time transferring the washing to filter paper. Wash the filter paper several times with water adjust the volume to 50ml with water and mix.

Aspirate the test solution and determine the absorbance in the same manner in which the instrument was calibrated.

If absorbance is above the range covered by calibration curve dilute an aliquot of sample to a suitable volume.

2.4.6 *Calculation*

Lead as Pb in ppm

Concentration X dil /wt of the sample.

Lead in Percentage Multiply the above with $100/10^6$

3 FREEDOM FROM LEAD

3.1 Outline of the Method

Determination of lead in lead-free paints is carried out by treating the ash of the paint with nitric acid and then with ammonium acetate solution, and precipitating lead as lead sulphide and finally oxidizing to lead sulphate.

3.2 Reagents

3.2.1 *Dilute Nitric Acid* — Lead-free, approximately 4 N.

3.2.2 *Ammonium Acetate Solution* — Lead-free, 10 percent *mlv*.

3.2.3 *Concentrated Sulphuric Acid* — Lead-free, sp gr 1.84.

3.2.4 *Dilute Sulphuric Acid* — 2 percent, obtained by dissolving 11 ml of concentrated sulphuric acid in one litre of water.

3.2.5 *Ammonium Acetate* — Solid, lead-free.

3.2.6 Hydrogen Sulphide — Gas, from Kipp's apparatus.

3.2.7 Hydrogen Sulphide Water —Saturated solution.

3.3 Procedure

Weigh 50 g of the material in a silica basin, and ash it carefully until only slight traces of carbon remain. The temperature of the basin shall not be allowed to rise above faint red heat, as at higher temperatures some lead may be lost by volatilization. Treat the ash so obtained with dilute nitric acid. The quantity of acid is immaterial provided it is sufficient to extract the soluble matter, but avoid too great an excess since it has to be vaporated off. Allow the basin to stand on a boiling water-bath for at least three hours. In case a large quantity of insoluble residue is left, heat the basin on the water-bath overnight. Decant off the supernatant liquid through a filter paper and extract the insoluble residue again on a boiling water-bath for one hour with dilute nitric acid. Filter through the same filter paper and wash the residue thoroughly on the filter paper with hot water. Treat the residue on the filter paper with 10 ml of ammonium acetate solution, filter and wash again. Mix the filtrate and washings in a 500-ml evaporating basin, add 2 ml of concentrated sulphuric acid and evaporate the contents of the basin on a sand-bath till fumes appear. Add 100 ml of water to the basin and allow to stand on the boiling water-bath for 15 minutes. Then dilute the contents to about 150 ml and allow to stand overnight at room temperature. Filter the insoluble matter on a No. 42 Whatman filter paper (9 cm) and wash thoroughly with dilute sulphuric acid. Transfer the filter paper and residue to a small beaker, cover with 20 ml of water, and add 1 to 2 g of ammonium acetate. Heat the beaker on the water-bath for not less than half an hour, stirring the contents occasionally. Decant the liquid through No. 42 Whatman filter paper (9 cm). Repeat the extraction with water and ammonium acetate. Transfer all the insoluble matter including the filter pulp to the filter and wash throughout with warm water collecting the filtrate and washings in a 150-ml beaker. Pass hydrogen sulphide through the liquid for 10 to 15 minutes and filter the precipitated lead sulphide at once through a No. 40 Whatman filter paper (9 cm). Wash thoroughly but quickly with hydrogen sulphide water keeping the residue on the filter paper, if any, covered with liquid till washing is completed. Transfer the precipitate and filter paper to a tared silica crucible. Dry, carefully ignite to sulphate, cool and weigh.

3.4 Alternatively, determine the quantity of lead by either of the following methods:

a) By electrolysis after dissolving the precipitated lead sulphide in nitric acid, or

b) By polarographic method.

3.5 Calculation — Calculate as lead (Pb) and express the result as percent of the mass of the material taken for test.

