*भारतीय मानक*
*Indian Standard*

**IS 16913 : 2018**

# प्रसाधन सामग्री के परीक्षण की पद्धतियाँ — भारी धातुएँ ज्ञात करना — परमाणवीय अवभाषण स्पेक्ट्रोमीटरी (ए.ए.एस.) द्वारा भारी धातुएँ (आर्सेनिक, कैडमियम, सीसा और पारा) ज्ञात करना

# Methods of Test for Cosmetics — Determination of Heavy Metals (Arsenic, Cadmium, Lead and Mercury) by Atomic Absorption Spectrometry (AAS)

ICS 71.040.50, 71.100.70

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**Price Group 2**

Cosmetics Sectional Committee, PCD 19

## FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Cosmetics Sectional Committee, had been approved by the Petroleum, Coal and Related Products Division Council.

In the formulation of this draft Indian Standard, considerable assistance has been taken from ACM THA 05 ‘Determination of Heavy Metals (Arsenic, Cadmium, Lead and mercury) in Cosmetic Products’.

Currently, Indian Standards on finished cosmetic products allow only the colorimetric method for determination of heavy metals as the method can be easily carried out without requirement of sophisticated instrumentation particularly to enable small scale cosmetic industry. Presently, worldwide some instrumental methods are available which provide sensitive and accurate results and also are faster than traditional test methods. Also, there is provision in Indian Pharmacopoeia (clause Alternative methods under General Notices) for use of alternative test methods that alternative methods of analysis may be used for control purposes, provided that the methods used are shown to give results of equivalent accuracy and enable an unequivocal decision to be made as to whether compliance with the standards would be achieved if the official methods were used.

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state and relies on the Beer-Lambert law.

In reporting the results 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*)’.

## *Indian Standard*

# METHODS OF TEST FOR COSMETICS — DETERMINATION OF HEAVY METALS (ARSENIC, CADMIUM, LEAD AND MERCURY) BY ATOMIC ABSORPTION SPECTROMETRY (AAS)

## 1 SCOPE

This standard covers the method for determination of heavy metals (arsenic, cadmium, lead and mercury) by Atomic Absorption Spectrometry (AAS) in finished cosmetic products and raw materials for cosmetics.

NOTE — It can be used as an alternate method to colorimetric method for testing heavy metals in finished cosmetic products and Raw materials for cosmetics on routine basis. However, in the event of any dispute, Colorimetric method shall be treated as referee method.

## 2 REFERENCES

The following standards contain provisions, which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

| *IS No.* | *Title* |
|---|---|
| 264 : 2005 | Nitric acid — Specification (*third revision*) |
| 265 : 1993 | Hydrochloric acid — Specification (*fourth revision*) |
| 1070 : 1992 | Reagent grade water — Specification (*third revision*) |

## 3 OUTLINE OF METHOD

Organic matter in sample is digested by wet digestion, dry digestion or high pressure microwave digestion and amount of heavy metals, that is arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) is determined using graphite furnace atomic absorption spectrophotometer (GF-AAS) and flow injection analysis system-atomic absorption spectrophotometer (FIAS-AAS).

## 4 REAGENTS

**4.1 Nitric Acid ($HNO_3$)**, *see* IS 264.

**4.2 Hydrochloric Acid (HCl)**, *see* IS 265.

**4.3 Hydrogen peroxide ($H_2O_2$)**, 30 percent (*v/v*).

CAUTION — Hydrogen peroxide is corrosive and irritant. Handle with great caution. Wear goggles of safety glass and gloves impervious to hydrogen peroxide for all operations where hydrogen peroxide is handled directly. Store it below 10 °C, preferably in refrigerator.

### 4.4 Reductant

For lead, either 1.1 percent (*w/v*) stannous chloride ($SnCl_2$) in 3 percent (*v/v*) hydrochloric acid or 0.2 percent (*w/v*) sodium borohydride ($NaBH_4$) in 0.05 percent sodium hydroxide (NaOH).

NOTE — Reductant has to be freshly prepared.

**4.5 Magnesium Nitrate**, 50 percent (*w/v*)

**4.6 Reagent Grade water**, *see* IS 1070.

### 4.7 Standard Calibration Solutions

As, Cd, Pb and Hg standard stock solutions of concentration 1 000 $\mu$g/ml.

NOTE — All commercially available GF-AAS or FIAS-AAS may not be sensitive to the calibration range given in this procedure. In such case calibration range needs to adjusted to the sensitivity of the instrument and Accuracy/Precision needs to established accordingly.

**4.7.1** *Arsenic*

**4.7.1.1** *Graphite furnace atomic absorption spectrophotometer (GF-AAS)*

Prepare arsenic standard calibration solutions of concentration 5, 10, 20, 30 and 50 $\mu$g/l in 0.5 percent (*v/v*) nitric acid, respectively.

**4.7.1.2** *Flow injection analysis system-atomic absorption spectrophotometer (FIAS-AAS) using hydride generation technique*

a) Prepare arsenic standard calibration solutions of concentration 1 µg/ml.
b) Pipette 200, 400, 600, 800 µl from arsenic standard calibration solution into separate 100 ml volumetric flasks and continue as **6.3**.

**4.7.2** *Cadmium*

Prepare cadmium standard calibration solution of concentration 0.5, 1, 2, 3 and 5 µg/l in 0.5 percent (*v/v*) nitric acid, respectively.

**4.7.3** *Lead*

Prepare lead standard calibration solutions of concentration 5, 10, 20, 30 and 50 µg/l in 0.5 percent (*v/v*) nitric acid, respectively.

**4.7.4** *Mercury*

Prepare mercury standard calibration solutions of concentration 0.5, 1, 2, 3 and 5 µg/l in 3 percent (*v/v*) hydrochloric acid, respectively.

### 4.8 Modifier for GF-AAS

**4.8.1** Modifier is used to reduce the matrix interference and increase the ashing temperature and atomized temperature to improve the sensitivity. Modifier should be added into the sample test solution and calibration standard solution before test.

**4.8.2** *For Arsenic*

1 000 µg/ml Paladium — modifier.

**4.8.3** *For Lead and Cadmium*

Mix 1:1 of 0.2 percent (*w/v*) magnesium nitrate hexahydrate [$Mg(NO_3)_2.6H_2O$] in 0.5 percent (*v/v*) nitric acid and 0.2 percent (*w/v*) ammonium dihydrogen phosphate $(NH_4)H_2PO_4$ in 0.5 percent (*v/v*) nitric acid.

### 4.9 Reagent for Pretreatment of Arsenic

Mix 1:1 of 10 percent (*w/v*) potassium iodide (KI) and 10 percent (*w/v*) ascorbic acid.

## 5 APPARATUS

### 5.1 Silica Dish

### 5.2 Muffle Furnace

### 5.3 Water Bath

### 5.4 Heating Mantle

### 5.5 Block Heater

**5.6 Digestion Tube**, 50 ml.

### 5.7 Refrigerator

### 5.8 Whatman Paper No. 1 and No. 40

### 5.9 Microwave Digestion

Condition—

| *Sample Type* (1) | *Max Power* W (2) | *Max Temperature* °C (3) | *Max Pressure* bar (4) | *Time* min (5) |
|---|---|---|---|---|
| Cream | 800 | 200 | 75 | 50 |
| Powder | 1 000 | 200 | 75 | 40 |
| Lipstick | 900 | 200 | 75 | 50 |

### 5.10 Quartz or Tetrafluoromethane (TFM) vessel, 50 ml

### 5.11 Graphite Furnace Atomic Absorption Spectrophotometer (As, Cd, Pb)

Condition –

| *Element* (1) | *Wave-length* nm (2) | *Pyrolysis* °C (3) | *Atomized Temperature* °C (4) | *Injection Volume* ml (5) |
|---|---|---|---|---|
| As | 193.7 | 1 250 | 2 100 | 20 |
| Cd | 228.8 | 550 | 1 550 | 20 |
| Pb | 283.3 | 550 | 1 550 | 20 |

### 5.12 Flow Injection Analysis System — Atomic Absorption Spectrophotometer (Hydride Generation Technique)

Condition—

| *Element* (1) | *Wave-length* nm (2) | *Reducing Agent* (3) | *Carrier* (4) | *Atomiza-tion Tempera-ture* °C (5) | *Injection Volume* µl (6) |
|---|---|---|---|---|---|
| As | 193.7 | 0.2 percent (*w/v*) $NaBH_4$ | 10 percent (*v/v*) HCl | 900 | 500 |

### 5.13 Flow Injection Analysis System — Atomic Absorption Spectrophotometer (Cold Vapour Technique)

Condition—

| *Element* (1) | *Wave-length* nm (2) | *Reducing Agent* (3) | *Carrier* (4) | *Atomiza-tion Tempera-ture* °C (5) | *Injectic Volum* µl (6) |
|---|---|---|---|---|---|
| Hg | 253.7 | 1.1 percent (*w/v*) $SnCl_2$ or 0.2 percent (*w/v*) $NaBH_4$ | 3 percent (*v/v*) HCl | 300 | 500 |

### 5.14 Electrodeless Discharge Lamp or Hollow Cathode Lamp

As, Cd, Pb, Hg.

## 6 PROCEDURE

### 6.1 Sample Preparation

**6.1.1** *Microwave Digestion* (*for As, Cd, Pb, Hg*)

**6.1.1.1** Accurately weigh, to the nearest mg in duplicate 0.15-0.20 g of sample into a high pressure resistance 50 ml quartz or TFM vessel. Avoid contact with the side of the vessel. Add 3 ml concentrated nitric acid and 30 percent hydrogen peroxide 1 ml by using graduated pipette. If sample contain talcum or pigment add concentrated hydrochloric acid 1 ml.

**6.1.1.2** Close the vessel lid. Leave for about 15 min to ensure complete reaction. Digest in microwave digestion system at the specified program.

**6.1.1.3** After cooling to room temperature, add reagent grade water 20 ml to the digested solution, rinse the inner wall and lid thoroughly. Filter through Whatman paper No. 1 into 50 ml volumetric flask and dilute to volume with reagent grade water.

**6.1.2** *Dry Ashing* (*for As, Cd, Pb*)

**6.1.2.1** Accurately weigh 2.5 g sample into a silica dish and add 3 ml of 50 percent (*w/v*) magnesium nitrate.

**6.1.2.2** Dry on the water bath and ash the residue first in the heating mantle until no more fume and then in the muffle furnace at 500 °C for 3 h.

**6.1.2.3** Cool, add 25 ml 6M hydrochloric acid, filter into a 50 ml volumetric flask and dilute to volume with water. For As, continue under **6.3**.

**6.1.3** *Wet Digestion* (*for Hg*)

**WARNING** — This technique involves a low recovery of Hg as compare to the microwave digestion technique.

**6.1.3.1** Accurately weigh 0.5 g sample into a digestion tube with screw cap and add 7 ml of concentrated nitric acid.

**6.1.3.2** Heat the sample solution in a block heater at 60°C maximum for at least 3 h.

**6.1.3.3** Cool and dilute to volume (50 ml) with water. Stand for 24 h in the refrigerator for cream and lipstick samples. Filter the solution through Whatman paper No. 40.

**6.1.3.4** The digested solutions are used for analysis by FIAS-AAS (cold vapour mercury technique).

### 6.2 Reagent Blank Preparation

Prepare the reagent blank as using procedure given in **6.1** but without adding the sample. Sample preparation can be carried out by either one of the following methods.

### 6.3 Pretreatment for Arsenic

**6.3.1** Pipette 10 ml each of reagent grade water (as standard blank), the reagent blank, the standard solutions and the sample solution into separate 100 ml volumetric flasks.

**6.3.2** Add 10 ml of concentrated hydrochloric acid and 10 ml of reagent for pretreatment of As (**4.9**) to each of the solutions and allow them to stand for 45 min at ambient temperature. Dilute to volume with water. The final concentrations of the standard solutions are 2.0, 4.0, 6.0 and 8.0 µg/l, respectively.

**6.3.3** These solutions are used for analyses by FIAS-AAS (hydride generation technique).

### 6.4 Calibration Curve

**6.4.1** Inject standard calibration solutions into the GF-AAS or FIAS-AAS (Cold vapour technique) or FIAS-AAS (Hydride Generation System) at the specified condition (**5.11** to **5.13**). Plot the response (absorbance or peak height or area) *versus* concentration of each standard solution.

**6.4.2** Inject sample solutions into GF-AAS or FIAS-AAS (Cold vapour technique) or FIAS-AAS (Hydride Generation System). Record the response and concentration (µg/l) of As, Cd, Pb, Hg in sample solution, then calculate µg/g of As, Cd, Pb, Hg in sample.

**6.4.3** When metal's content is higher than the determination unit listed in respective Indian Standard, the sample extract (**6.1**) shall be diluted to concentration within the calibration range.

## 7 CALCULATION

$$\text{As/Cd/Pb/Hg, parts per million} = \frac{C \times V}{W \times 1\,000}$$

where

$C$ = concentration of As/Cd/Pb/Hg in sample solution, in µg/l;

$V$ = volume, of sample, in ml; and

$W$ = weigh, of sample, in g.

## 8 REMARKS

### 8.1 Precision

As given in Table 1.

### 8.2 Accuracy

Percent recovery of As, Cd, Pb and Hg from spiked cream are 84-86 percent, 66-71 percent, 85-99 percent and 95-108 percent, respectively.

### 8.3 Linearity and Range

Linearity of response over the range of concentration are as given in Table 2.

## Table 1

(*Clause* 8.1)

| **Metal** | **Content in Cream (µg/g)** | **Percent Relative Standard Deviation** | | **p-Value (n1 = n2 = 5, α = 0.05) Different Analysts** |
|---|---|---|---|---|
| | | Within Day | Different Days | |
| (1) | (2) | (3) | (4) | (5) |
| As | 10 | 10 | 15 | 0.47 |
| Cd | 1 | 10 | 10.0 | 0.09 |
| Pb | 40 | 5 | 4 | 0.49 |
| Hg | 1 | 15 | 25 | 0.22 |

## Table 2

(*Clause* 8.3)

| **Metal** | **Range** µg/l | **Correlation Coefficient** *r* |
|---|---|---|
| (1) | (2) | (3) |
| As | 5.0-50 | 0.999 21 |
| Cd | 0.5-5.0 | 0.999 97 |
| Pb | 5.0-50 | 0.999 25 |
| Hg | 0.5-5.0 | 0.998 15 |

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