(Reaffirmed 2014)
(Reaffirmed 2018)

भारतीय मानक

इलेक्ट्रोथरमल ऐटोमिक ऑबजोरपशन स्पेक्ट्रोमेट्री पद्धति द्वारा पानी में एन्टीमनी, लोहा व सेलेनियम ज्ञात करना

Indian Standard

DETERMINATION OF ANTIMONY, IRON AND SELENIUM IN WATER BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRIC METHOD

ICS 13.060.50

B U R E A U   O F   I N D I A N   S T A N D A R D S
MANAK   BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

May 2003

Price Group 3

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Drinks and Carbonated Beverages Sectional Committee had been approved by the Food and Agriculture Division Council.

This standard is based on electrothermal atomic absorption spectrometry to detect micro quantities of antimony, selenium and iron in water. This method is used for the determination of these elements in packaged water namely IS 13428 : 1998 'Packaged natural mineral water— Specification (first revision)' and IS 14543 : 1998 'Packaged drinking water (other than packaged natural mineral water) — Specifications'. In the preparation of this standard, considerable assistance has been derived from standard methods for the examination of water and waste water published by American Public Health Association, Washington, USA, 20th edition, 1998.

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)'.

Indian Standard

DETERMINATION OF ANTIMONY, IRON AND SELENIUM IN WATER BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRIC METHOD

1 SCOPE

This standard prescribes the determination of micro quantities of antimony, iron and selenium in water by Electrothermal Atomic Absorption Spectrometric Method.

2 APPARATUS

2.1 Atomic Absorption Spectrometer

Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment. The instrument must have background correction capability.

2.2 Source Lamps

Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally provide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

2.3 Graphite Furnace

Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating programme that provides sufficient thermal energy to atomize the elements of interest. Furnace heat controllers with only three heating steps are adequate for fresh waters with low dissolved solids content. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

2.4 Readout

Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computer capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

2.5 Sample Dispensers

Use microlitre pipettes (5 to 100 µl) or an automatic sampling device designed for the specific instrument.

2.6 Vent

Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapours, protects the instrument from corrosive vapours, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer. In laboratory locations with heavy particulate air pollution, use clean laboratory facilities, such as commercially available laminar-flow, clean-air benches or custom-designed work stations and analyze blanks that reflect the complete procedure.

2.7 Cooling Water Supply

Cool with tap water flowing at 1 to 4 l/min or use a recirculating cooling device.

2.8 Membrane Filter Apparatus

Use an all-glass filtering device and 0.45 µm or smaller pore-diameters membrane filters. For trace analysis of aluminum, use polypropylene or TFE devices.

3 REAGENTS

3.1 Metal-Free Water—Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample; single distillation, redistillation or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts.

3.2 Hydrochloric Acid, HCl conc — 50 percent.

3.3 Nitric Acid, HNO3 conc — 50 percent.

3.4 Matrix Modifier Stock Solutions

3.4.1 *Magnesium Nitrate*, 10 000 mg Mg/litre

Dissolve 10.5 g $Mg(NO_3)_2.6H_2O$ in water. Dilute to 100 ml with water.

3.4.2 *Nickel Nitrate*, 10 000 mg Ni/litre

Dissolve 4.96 g $Ni(NO_3)_2.6H_2O$ in water. Dilute to 100 ml with water.

3.4.3 *Phosphoric Acid*, 10 percent *(v/v)*

Add 10 ml conc H_3PO_4 to water. Dilute to 100 ml with water.

3.4.4 *Palladium Nitrate*, 4 000 mg Pd/litre

Dissolve 8.89 g $Pd(NO_3)_2$. H_2O in water. Dilute to 1 litre with water.

3.4.5 *Citric Acid*, 4 percent

Dissolve 40 g citric acid in water. Dilute to 1 litre with water.

3.5 Stock Metal Solutions

3.5.1 *Antimony*

Dissolve 0.266 9 g K(SbO) $C_4H_4O_6$ in water, add 10 ml of 50 percent HCl with water. 1 ml of this solution = 100 µg Sb.

3.5.2 *Iron*

Dissolve 0.100 g iron wire in a mixture of 10 ml of 50 percent HCl and 3 ml of concentrated HNO_3. Add 5 ml of concentrated HNO_3 and dilute to 1 000 ml with water. 1 ml of this solution = 100 µg Fe.

3.5.3 *Selenium*

Dissolve 2.190 g sodium selenite, Na_2SeO_3, in water containing 10 ml concentrated HCl and dilute to 1 litre. 1 ml of this solution = 1.00 mg Se.

3.6 Chelating Resin

100 to 200 mesh purified by heating at 60°C in 10 N NaOH for 24 h. Cool resin and rinse 10 times each with alternating portions of 1N HCl, metal-free water, 1N NaOH and metal free water.

4 PROCEDURE

4.1 Sample Pretreatment

Before analysis, pretreat all samples as indicated below. Rinse all glassware with 50 percent HNO_3 and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. Drinking waters (or natural mineral water), may be analyzed directly by atomic absorption spectroscopy for total metals without digestion. On collection acidify such samples to $pH<2$ with concentrated nitric acid (1.5 ml HNO_3 is usually adequate for drinking water) and analyze directly. For further verification or if changes in existing matrices are encountered, compare digested and undigested samples to ensure comparable results.

4.1.1 *Total Recoverable Metals* (Sb and Fe)

Quantitatively transfer undigested/ digested sample to a 100 ml volumetric flask, add an appropriate amount of matrix modifier (*see* Table 1), and dilute to volume with water. The digestion procedure is outlined in Annex A for iron and in Annex B for antimony.

4.1.2 *Total Recoverable Metals* (Se)

Transfer 100 ml of shaken sample, 1 ml conc HNO_3, and 2 ml 30 percent H_2O_2 to a clean, acid-washed 250 ml beaker. Heat on a hot plate without allowing solution to boil until volume has been reduced to about 50 ml. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (*see* Table 1) and dilute to volume in a 100 ml volumetric flask with water. Substitution of palladium is uneconomical. Nickel may be deleted if palladium is co-added during analysis. Simultaneously prepare a digested blank by substituting water for sample and proceed with digestion as described above.

Table 1 Potential Matrix Modifiers for Electrothermal Atomization Atomic Absorption Spectrometry

(Clauses 4.1.1 and 4.1.2)

Modifier	Analysis for which Modifier may be Useful
(1)	(2)
1 500 mg Pd/litre + 1 000 mg $Mg(NO_3)_2$/litre	Sb, Se
5 000 mg $Mg(NO_3)_2$/litre	Fe
50 mg Ni/litre	Se

4.2 Instrument Operation

4.2.1 Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelength longer than 350 nm. If background

correction above 350 nm is needed, deuterium arc background correction is not useful and other types must be used.

4.2.2 Select proper inert or sheath gas flow. In some cases, it is desirable to interrupt the inert gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapour in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions.

4.2.3 To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

4.2.4 Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

4.2.5 Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

4.2.6 The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50°C to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature *versus* sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

4.3 Instrument Calibration

4.3.1 Prepare standard solutions for instrument calibration by diluting metal stock solutions. Prepare fresh standard solutions daily.

4.3.2 Prepare a blank and at least three calibration standards in the appropriate concentration range (*see* Table 2) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

4.3.3 Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in triplicate to verify method precision.

4.3.4 Construct an analytical curve by plotting the average peak absorbances or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

4.4 Sample Analysis

Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85 percent to 115 percent for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of <10 percent is considered acceptable reproducibility. Average replicate values.

4.4.1 *Direct Determination*

Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Usually add modifier immediately after the sample, preferably using an automatic sampler or a micropipette. Some methods require modifier to be injected before the sample. Use the same volume and concentration of modifier for all standards and samples. Dry, char and atomize according to the preset programme. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the sample is greater than absorbance (or concentration)

Table 2 Detection Levels and Concentration Ranges for Electrothermal Atomization Atomic Absorption Spectrometry

(*Clause* 4.3.2)

Element	Wavelength nm	Estimated Detection Limit μg/l	Optimum Concentration Range μg/l
(1)	(2)	(3)	(4)
Sb	217.6	3	20-300
Fe	248.3	1	5-100
Se	196.0	2	5-100

or peak area of the most concentrated standard solution, dilute sample and reanalyze. If very large dilutions are required, another technique (for example, flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if present in the solutions) constant. Dilute the sample in a blank solution of acid and matrix modifiers.

4.4.2 *Method of Standard Additions*

Refer to **4.3**. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset programme. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination.

Using linear graph paper, plot average absorbance or instrument response for the sample and the additions on the vertical axis against the concentrations of the added element on the horizontal axis, using zero as the concentration for the sample. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the negative of the element concentration in the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

5 CALCULATIONS

5.1 Direct Determination

$$\mu g \ metal/l = C \times F$$

where

C = metal concentration as read directly from the instrument or from the calibration curve, $\mu g/l$, and

F = dilution factor.

5.2 Method of Additions

$$\mu g \ metal/l = C \times F$$

where

C = metal concentration as read from the method of additions plot, $\mu g/l$; and

F = dilution factor.

ANNEX A

(*Clause* 4.1.1)

NITRIC ACID DIGESTION

A-1 APPARATUS

A-1.1 Hot Plate

A-1.2 Conical (Erlenmeyer) Flasks — 125 ml or Griffin Beakers — 150 ml, acid washed and rinsed with water.

A-1.3 Volumetric Flasks — 100 ml.

A-1.4 Watch Glasses — Ribbed and unribbed.

A-2 REAGENT

A-2.1 Nitric Acid, HNO₃ — Concentrated, analytical or trace metal grade.

A-3 PROCEDURE

Transfer a measured volume (100 ml recommended) of well-mixed, acid preserved sample appropriate for the expected metal concentrations to a flask or beaker.

In a hood, add 5 ml concentrated HNO_3. If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels are being determined. Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 ml to 20 ml) before precipitation occurs. Continue heating and adding concentrated HNO_3 as necessary until digestion is complete as shown by a light coloured, clear solution. Do not let sample dry during digestion.

Wash down flask or beaker walls and watch glass cover (if used) with metal-free water and then filter, if necessary. Transfer filtrate to a 100 ml volumetric flask with two 5 ml portions of water, adding these rinsings to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

ANNEX B

(Clause 4.1.1)

NITRIC ACID- HYDROCHLORIC ACID DIGESTION

B-1 APPARATUS

Same as in **A-1**. Steam bath may also be needed.

B-2 REAGENTS

B-2.1 Nitric Acid, HNO₃ — Concentrated, analytical or trace metal grade.

B-2.2 Hydrochloric Acid, HCl — 50 percent.

B-2.3 Nitric Acid, HNO₃ — 50 percent.

B-3 PROCEDURE

B-3.1 Transfer a measured volume of well-mixed, acid preserved sample appropriate for the expected metal concentrations to a flask or beaker. In a hood, add 3 ml concentrated HNO₃ and cover with a ribbed watch glass. Place flask or beaker on a hot plate and cautiously evaporate to the less than 5 ml, making certain that sample does not boil and no area of the bottom of the container is allowed to go dry. Cool. Rinse down walls of beaker and watch glass with a minimum of metal-free water and add 5 ml concentrated HNO₃. Cover container with a unribbed watch glass and return to hot plate. Increase temperature of hot plate so that a gentle reflux action

occurs. Continue heating, adding additional acid if necessary, until digestion is complete (generally indicated when the digestate is light in colour or does not change in appearance with continued refluxing). Cool. Add 10 ml 50 percent HCl and 15 ml water per 100 ml of anticipated final volume. Heat for an additional 15 min to dissolve any precipitate or residue. Cool. Wash down beaker walls and watch glass with metal-free water, filter to remove insoluble material that could clog the nebulizer and transfer filtrate to a 100 ml volumetric flask with rinsings. Alternatively centrifuge or let settle overnight. Adjust to volume and mix thoroughly.

B-3.2 For this less rigorous digestion procedure, transfer a measured volume of well-mixed, acid-preserved sample to a flask or beaker. Add 2 ml 50 percent HNO₃ and 10 ml 50 percent HCl and cover with a ribbed watch glass. Heat on a steam bath or hot plate until volume has reduced to near 25 ml making certain sample does not boil. Cool and filter to remove insoluble material or alternatively centrifuge or let it settle overnight. Quantitatively transfer sample to volumetric flask, adjust volume to 100 ml and mix.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act,* 1986 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

BIS has the copyright of all its publications. No part of these publications may be reproduced in any form without the prior permission in writing of BIS. This does not preclude the free use, in the course of implementing the standard, of necessary details, such as symbols and sizes, type or grade designations. Enquiries relating to copyright be addressed to the Director (Publications), BIS.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the latest issue of 'BIS Catalogue' and 'Standards: Monthly Additions'.

This Indian Standard has been developed from Doc : No. **FAD 14 (1324).**

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters :

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110 002
Telephones : 2323 0131, 2323 33 75, 2323 9402

Telegrams : Manaksanstha
(Common to all offices)

Regional Offices :   Telephone

Central	: Manak Bhavan, 9 Bahadur Shah Zafar Marg NEW DELHI 110 002	$\begin{cases} 2323\ 7617 \\ 2323\ 3841 \end{cases}$
Eastern	: 1/14 C.I.T. Scheme VII M, V. I. P. Road, Kankurgachi KOLKATA 700 054	$\begin{cases} 2337\ 8499, 2337\ 8561 \\ 2337\ 8626, 2337\ 9120 \end{cases}$
Northern	: SCO 335-336, Sector 34-A, CHANDIGARH 160 022	$\begin{cases} 60\ 3843 \\ 60\ 9285 \end{cases}$
Southern	: C.I.T. Campus, IV Cross Road, CHENNAI 600 113	$\begin{cases} 2254\ 1216, 2254\ 1442 \\ 2254\ 2519, 2254\ 2315 \end{cases}$
Western	: Manakalaya, E9 MIDC, Marol, Andheri (East) MUMBAI 400 093	$\begin{cases} 2832\ 9295, 2832\ 7858 \\ 2832\ 7891, 2832\ 7892 \end{cases}$

Branches : AHMEDABAD. BANGALORE. BHOPAL. BHUBANESHWAR. COIMBATORE. FARIDABAD. GHAZIABAD. GUWAHATI. HYDERABAD. JAIPUR. KANPUR. LUCKNOW. NAGPUR. NALAGARH. PATNA. PUNE. RAJKOT. THIRUVANANTHAPURAM. VISAKHAPATNAM.