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भारतीय मानक मसौदा

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भाग 25 अमोनिया

[*IS 5182 (भाग 25) का पहला पुनरीक्षण*]

Draft Indian Standard

Air Pollution — Methods for Measurement

Part 25 Ammonia

[*First revision of IS 5182 (Part 25)*]

ICS 13.040.20

Air Quality Sectional Committee, CHD 35	**Last Date for Comments**: 21st December 2024

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FOREWORD

(*Formal clause will be added later*)

The undesired impacts of pollutants on flora and fauna are of high concern to scientists and technologists, in particular, and to common people, in general. Ammonia is one such pollutant. Gaseous ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. The largest source of NH_3 emissions is agriculture, including animal husbandry and NH_3-based fertilizer applications. Other sources of NH_3 include industrial processes, vehicular emissions and volatilization from soils and oceans.

Atmospheric ammonia presents three major environmental issues:

a) Odor – Ammonia has a strong and unpleasant odor.

b) Ammonia at high levels is toxic to humans and animals. It is known to cause irritation to skin, eyes and respiratory tract.

c) Ammonia reacts with atmospherically formed sulfuric and nitric acids and forms precipitated salts which contribute to ambient level of fine particles.

Keeping the above in mind, proper methodology to accurately determine the concentration of ammonia in ambient atmosphere is of utmost importance. This standard describes Indophenol method for the measurement of ammonia in ambient air.

This standard was first published in 2018. This first revision has been taken up in order to bring out the standard

in latest style and format of the Indian Standards. The relevant clauses and test methods have been added and the references have been updated.

In this revision following modifications have been done:

a) Period of sampling is reviewed in line with NAAQS;

b) Monitoring in 3 shifts of 8 hour is recommended for 24 h instead of drawing 24, one-hour samples as it has practical issues;

c) Apparatus clause has been updated; and

d) New clause for Quality Control Measures has been included.

This Indian Standard is published in several parts. The other parts in this series are:

Part 1 Dust fall (*first revision*)
Part 2 Sulphur Dioxide
  Sec 1 Tetrachloromercurate Pararosaniline method
  Sec 2 Ultraviolet fluorescence method
Part 3 Radioactivity (particulate in air)
Part 4 Suspended particulate matter (*first revision*)
Part 5 Sampling of Gaseous Pollutants (*first revision*)
Part 6 Oxides of nitrogen (*first revision*)
    Sec 2 chemiluminescence method
Part 7 Hydrogen sulphide (*first revision*)
Part 8 Sulphation rate
Part 9 Oxidants
Part 10 Carbon monoxide (*first revision*)
Part 11 Benzene, toluene and xylene (BTX) (*second revision*)
Part 12 Polynuclear aromatic hydrocarbons (PAHs) in air particulate matter (*first revision*)
Part 13 Total fluorides in ambient air
Part 14 Guidelines for planning the sampling of atmosphere (*second revision*)
Part 15 Mass concentration of particulate matter in the atmosphere
  Sec 2 Beta-ray absorption method
Part 16 Recommended practice for collection by filtration and determination of mass, number and optical sizing of atmospheric particulates
Part 17 C1 to C2 hydrocarbons in air by gas chromatography
Part 18 Continuous analysis and automatic recording of the oxidant content of the atmosphere
Part 19 Chlorine (*first revision*)
Part 20 Carbon Disulphide
Part 21 Non methane hydrocarbons in air by gas chromatography
Part 22 Lead
Part 23 Respirable suspended particulate matter (PM 10), cyclonic flow technique
Part 24 Fine Particulate Matter (PM 2.5)
Part 26 Nickel
Part 27 Vapor-Phase Organic Chemicals Vinyl Chloride to nc22 Hydrocarbons in air and Gaseous Emissions by Diffusive (Passive) Sampling onto Sorbent Tubes or Cartridges Followed by Thermal Desorption (TD) and Capillary gas Chromatography (GC) Analysis.
Part 28 Vapor - Phase Organic Chemicals C3 to nC30 Hydrocarbons in Air and Gaseous Emissions – Sampling by Pumped Sorbent Tubes Followed by Thermal Desorption (TD) and Capillary gas Chromatography (GC) Analysis. (*Under Preparation*)
Part 29 Vapor Phase Mercury in Ambient Air
Sec 1 Cold-Vapor Atomic Fluorescence Spectrometer method by Amalgamation Principle (*Under Preparation*)
Sec 2 Cold-Vapor Atomic Absorption or Fluorescence Spectroscopy CVAFS Method Using Acidified solution of KMnO4 Principle (*Under Preparation*)

Part 30 Metals in Particulate Matter in Ambient Air (*Under Preparation*)

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 2:2022 'Rules for rounding off numerical values (second revision)'.

Indian Standard

Air Pollution — Methods for Measurement

Part 25 Ammonia

(*First Revision*)

1 SCOPE

This standard prescribes the Indophenol method for measurement of ammonia in ambient air.

2 REFERENCE

The standards listed in Annex A 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 Indian standard are encouraged to investigate the possibility of applying the most recent editions of the standards.

3 TERMINOLOGY

For the purpose of this standard the definitions given in IS 4167 shall apply.

4 PRINCIPLE

Ammonia in the atmosphere is collected by bubbling a measured volume of air through a dilute solution of sulfuric acid to form ammonium sulfate. The ammonium sulfate formed in the sample is analyzed calorimetrically by reaction with phenol and alkaline sodium hypochlorite to produce indophenol, a blue dye. The reaction is accelerated by the addition of sodium nitroprusside as catalyst.

5 RANGE AND SENSITIVITY

5.1 With a sampling rate of 1 l/min, a concentration range of 20 $\mu g/m^3$ to 700 $\mu g/m^3$ in air may be determine with a sampling time of 1 h.

5.2 The lower limit of detection of the analysis is 0.2 μg NH_3/ml.

6 INTERFERENCES

6.1 Prefilters may remove some gaseous ammonia but if prefilters are not used, the method will determine both gaseous ammonia and ammonium contained in particulates

6.2 Ferrous, chromous, and manganous ions if present in mg amounts cause positive interference in the analytical procedure because of precipitation. Copper ions inhibit color development strongly and therefore cause negative interference. Addition of Ethylene Diamine Tetraacetic Acid (EDTA) prevents these effects. Nitrite and sulfite interfere if present in 100 fold excess. Based on tests with solutions, formaldehyde causes a negative interference of 10to 15percent.

6.3 Interfering particulate matter in the air can be removed by filtration of the air sample.

7 APPARATUS

7.1 Gas sampler to absorb ammonia from air in impingers shall consist of the following:

7.1.1 *Cabinet —* The cabinet can be of the following two types:

   a) Type-I: Cabinet with built in sampling pump; and

   b) Type-II: Cabinet without sampling pump in which case the suction for sampling the gases is provided by the blower/pump of particulate sampler. Except the sampling pump, both Type-I/II cabinets should be designed to suitably hold items as listed from **7.1.1.1**to **7.1.1.8**.

7.1.1.1 Sampling pump whether built in or external should be capable of sucking unfiltered air and capable of maintaining flow rate of 10 l/min free flow with pulse dampening system.

7.1.1.2 *Cold box*

A cold box capable of holding 4 impingers capable of thermoelectrically maintaining temperature of absorbing reagents in impingers during sampling at 15 °C ± 5 °C. This is requiredfor optimum absorption of gases in absorbing reagent as well as to avoid loss of absorbing reagent by evaporation during sampling in the summer season. The cold box housing shouldbe insulated and deep enough to cover the impingers up to the level of absorbing solution foreffective temperature control around absorbing solutions.

7.1.1.3 The cabinet shall have a digital temperature indicator cum controller with a resolutionof 0.1°C and accuracy of ± 1°C to continuously monitor and display the temperature of impinger sampling reagents.

7.1.1.4 *Arrangement for measurement, control and distribution of flow*

A rotameter shall be used for flow measurement with a range of 0 lpm to 1.5 lpm with resolution of 0.05 liter/min and accuracy of ± 2 percent full scale. The system will have four inlets individually connected to the outlet of each impinger on one end and other end to flowcontrol valve via particulate trapping filters. Outlet of the manifold unit shall be connected to the suction pump. Material of control valves of the manifold should be made up of non-corrosive metal. Entire sampling line and a manifold shall be leakage free. Leak check system must be integral part of the sampling unit.

7.1.1.5 *Impingers*

All glass standard 35 ml midget impinger with dimensions as shown in Fig.1 shall be used for sampling. The glass impingers shall be made from class HGB3 glass conforming to IS 2303 (Part l/Sec 1).

7.1.1.5.1 *Prefilter and Prefilter Holder*

A 25 mm 2-piece air sampling plastic cassette preloaded with glass fiber filter which can beconnected in line before the impinger. If prefilters are not used, the method will determine both gaseous ammonia and ammonium contained in particulates

7.1.1.6 *Timer and time totalizer*

The sampler shall have arrangement for run time display using a time totalizer with 1 sec resolution resettable/cumulative. It shall also have a 24 h programmable timer to automatically shut off the system after pre-set interval.

7.1.1.7 *Connecting tubing*

All tubing for interconnections shall be of inert silicon tube.

7.1.1.8 *Power supply and cords*

The system should work at 230 V A.C and power cords for supplying the power from the plugto the machine should be provided. The cabinet can also have an on/off switch.

7.1.2 The dimensions, finish and material of the cabinet and housing of the items in cabinet is at manufacturers discretion other than as defined in **7.2** but to ensure that it is sturdy, compactand light weight for outdoor field use as well as access or tempering is restricted. The cabinetcan have pedestals to hold it stable on surface it is placed. The placings of the items be done ina manner that is practical and easy to use.

7.2 Spectrophotometer

A spectrophotometer suitable for measurement of absorbance at 630 nm with an effective spectral band width of not more than 5 nm is required with wavelength accuracy of 2 nm or less. Problems may occur with spectrophotometer having greater spectral band widths. The wavelength calibration of the instrument shall be verified. If transmittance (*T*) is measured, this can be converted to absorbance (*A*) by the formula:

$$A = Log_{10}(1/T)$$

7.3 Glassware

Borosilicate and low actinic (amber colour) glassware or plasticware of equivalent quality as applicable.

7.4 Balance

An analytical balance with readability of 0.1 mg or better. The installation of balance shall be as per manufacturer's instruction on a vibration dampening surface.
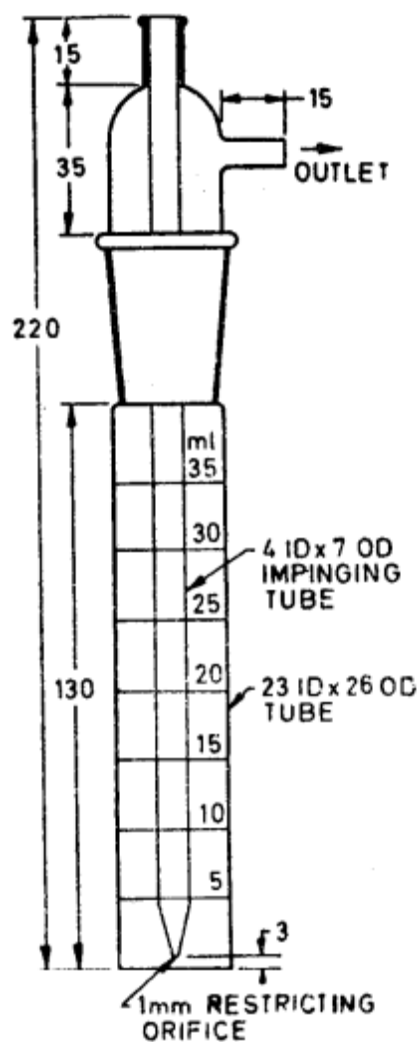
FIG.1 IMPINGER

8 REAGENTS

Quality of all reagents shall be analytical reagent grade, unless specified otherwise.

8.1 Reagent Grade Water

Reagent grade water of grade 2 minimum as per IS 1070 shall be used. The water should be ammonia free.

8.2 Absorbing solution

Dilute 3.0 ml of concentrated sulphuric acid (H_2SO_4) (18 M) (*see* IS 266) to 1 litre withwater to obtain 0.1 N sulphuric acid (H_2SO_4)

8.3 Sodium Nitroprusside [Sodium Nitrosylpentacyanoferrate (III)]

Dissolve 2 g sodium nitroprusside in 100 ml of water. The solution keeps well in the refrigerator for 2 months. (0.02gm/ml)

8.4 Sodium Hydroxide, 6.75 M

Dissolve 270 g sodium hydroxide (*see* IS 376) in about 1 l of distilled water. Boil down to 600 ml in order to volatilize the ammonia contained in the reagent. Cool and make up thevolume to 1 l using ammonia free reagent water (**8.1**). Store in polyethylene bottle.

CAUTION: This solution is extremely caustic. Prevent contact with skin or eyes.

8.5 Sodium Hypochlorite Solution (0.1 N)

Dilute 5 percent to 6 percent analytical reagent sodium hypochlorite with distilled water to give a 0.1 N solution (3.7 percent). The solution keeps well for 2 months in a refrigerator.

8.5.1 *Standardization of Sodium Hypochlorite Solution*

8.5.1.1 Acidic iodide solution

Dissolve 7 g potassium iodide (KI) in 20 ml glacial acetic acid and make up the volume to 1000 ml with distilled water.

8.5.1.2 *Standard sodium thiosulphate solution (0.1 N)*

Prepare a stock solution by taking 25 g of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$)in a beaker, add 0.1 g of sodium carbonate, and dissolve using reagent grade water (freshly boiled and cooled) making the solution up to a final volume of 1 l. Allow the solution to standone day before standardizing.

8.5.1.2.1 To standardize, accurately weigh, to the nearest 0.1 mg, 1.5 g of potassium iodate(KIO_3) certified reference material dried at 180 °C, dissolve, and dilute to 500 ml in a volumetric flask. Pipette 50 ml of the potassium iodate solution (0.1 N) into a 250 ml stoppered conical flask. Then add 2 g potassium iodide and 10 ml (1 : 10) hydrochloric acid to the flaskand immediately stopper it. After 5 min, titrate with the stock thiosulphate solution to a paleyellow (straw) color. Add a few drops of starch solution and continue titration until the bluecolour disappears. Note the titre value. Calculate the strength of the stock thiosulphate solution using normality equation:

$$N_1 \times V_1 = N_2 \times V_2$$

where,

$V1$ = Volume of potassium iodate solution taken, that is, 50 ml;

$N1$ = Strength of potassium iodate solution, that is, 0.1 N;

$V2$ = Volume of thio-sulphate solution consumed (titre value); and

$N2$ = Strength of the stock-thiosulphate solution.

8.5.1.3 Take 50 ml acidic iodide solution in a conical flask. Add 1 ml sodium hypochloritesolution. Titrate against 0.1 N sodium thiosulphate solution (**8.5.1.2**) till yellow colour appears. Add starch solution and titrate till colorless. Note the burette reading.

8.5.1.4 *Calculation*

$$Normality\ of\ NaOCl = \frac{(BR \times Normality\ of\ Na_2S_2O_3)}{Volume\ of\ NaOCl\ in\ ml}$$

where,

BR = burette reading.

8.6 Phenol Solution 45 Percent (v/v)

Melt phenol (Grade A, *see* IS 538) by immersing a bottle containing the material in a waterbath at 60 °C. Pour 45 ml (50 g) in to a 100 ml warmed cylinder and fill to mark with methanol.

8.6.1 *Buffer*

Dissolve 50 g of sodium phosphate dodecahydrate ($Na_3PO_4.12H_2O$) and 74 ml of 6.75 Msodium hydroxide (NaOH) in distilled water and make up the volume to 1 l with distilled water.

8.6.2 *Working Hypochlorite Solution*

Mix 30 ml of 0.1 N sodium hypochlorite and 30 ml of 6.75 M Sodium hydroxide and dilute to 100 ml with distilled

water. Prepare fresh daily.

8.6.3 *Working Phenol Solution*

Mix 20 ml of the 45 percent Phenol solution with 1 ml of 2 percent Sodium nitroprusside and dilute to 100 ml with distilled water.

8.7 Ammonia Standard Solution

8.7.1 *Ammonia stock Solution*

Dissolve 3.18 g of ammonium chloride (NH_4Cl) or 3.88 g of ammonium sulphate [$(NH_4)_2SO_4$] (Certified reference material) in 1 l of distilled water [1 ml equal to 1 mg ammonia (NH_3)]. Add a drop of chloroform ($CHCl_3$) for better preservation. The solution is stable for 2 months.

8.7.2 *Ammonia Working Solution*

Dilute 10 ml of the stock solution to 1 l with absorbing solution in a volumetric flask [1ml equal to 10 µg ammonia (NH_3)]. Prepare daily with distilled water.

8.8 Glass Cleaning Solution

Dilute 10 ml of concentrated hydrochloric acid (HCl) (12 M) (*see* IS 265) to 100 ml with distilled water (molarity approximately 1.2 M).

NOTE — Certified reference material with certified value and associated uncertainty provided by an IS/ISO 17034 accredited reference material producer with stated metrological traceability to SI units shall be used as applicable.

9 SAMPLING

The sampling for NH_3 is specified in Table 1.

Table 1 Sampling for NH₃

(*Clause* 9)

Sl No.	Pollutant	Time Weighted Average	Concentration in Ambient Air	
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (Notified by Central Government)
(1)	(2)	(3)	(4)	(5)
i)	Ammonia (NH_3) µg/m³, (micrograms per cubic meter of air)	Annual 24 h	100 400	100 400

NOTE — One can select other combinations of duration, period and frequency to meet objectives of the sampling with corresponding adjustments in flow rate and absorbing solution in impinger to maintain linearity between absorbance and concentration

9.1 Location of Sampling Station/Sampler

For planning of network of sampling stations including number of stations and location of sampling station or sampler refer IS 5182 (Part 14). Record topographical features, sources of pollution, any obstructions to sampling station including any deviations specific to site and with relevance to objectives of monitoring on the sampling sheet.

9.2 The sample shall be drawn as specified in Table 2.

Table 2 Frequency of Drawing Sample

(*Clause* 9.2)

Sl No.	Duration	Period	Frequency	Flow Rate, l/min	Absorbing Solution in Impinger, in ml
(1)	(2)	(3)	(4)	(5)	(6)
i)	24 h	8 h	3 Shifts	1	25
ii)	Annual	24 h	104 Measurements	1	25
			8 h × 3 shifts		

NOTES

1) Annual arithmetic means of minimum 104 measurements in a year at a particular site taken twice a week 24 h at uniform intervals.
2) Since practically sometimes it may not be possible to target sampling of 24 h in a day or 104 measurements in a year due to power failure or other site-specific problems, the values monitored for 75 percent of the time and more can be considered as representative NH_3 values in the ambient air.

9.3 Operation of Sampler

9.3.1 The manufacturer's instructions are to be followed.

9.3.1.1 The sampling shall be done as follows:

a) Carry requisite quantity of absorbing solutions to sampling site in chemical resistant HDPE bottles with leak-proof polypropylene screw cap meant for the purpose of packing, shipping and storage in insulated box; Impingers should be capped during transportation.

b) Place standard 35 ml midget impinger in gas sampler. Impingers shall be cleaned before each sampling to remove deposited chemicals on surfaces and clogging chemical residues at impinger midget tube. To make impinger leak proof silicon grease must be applied at joint of impinge;

c) Impingers shall be verified for (i) pore size of the midget and (ii) gap between midget and bottom, to maintain absorbing efficiency at such intervals as decided by laboratory depending upon use. The verification can be done using calibrated master kit supplied by the manufacturer for the purpose.

d) Add 25 ml absorbing solution to the impinger;

e) Run sampler for such period and frequency as prescribed in the standard;

f) Record initial time totalizer reading;

g) Switch on the sampler;

h) Record initial flow rate;

j) Monitor flow rate during sampling. Record flow rate at regular intervals. If flow rate varies from set value by more than 15 percent stop the sampling. The sampler may need service and recalibration before using again;

k) At the end of sampling period and frequency record final flow rate;

l) Switch off the sampler;

m) Record final time totalizer reading;

n) Record reasons any loss of time due to power failure or any other malfunctions;

o) Check loss of water from absorbing reagent in impinger and make it up using reagent grade water (Grade-2) before transferring it into sample storage bottle at site;

p) Transfer sample storage bottle to lab in insulated box; and

q) In laboratory, store the sample in a refrigerator at 5° C or less. It has been observed that if the collected

impinger solutions are stored for 2 days, precision of the method is lowered significantly.

10 PROCEDURE

10.1 Preparation of standards

Pipette 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the working standard solution into 25 ml glass stoppered volumetric flasks and bring volume to 10 ml by adding 9.5, 9.0, 8.5, 8.0 and 7.5 ml absorbing solution in each flask respectively. Further fill to 25 ml mark by add reagentsto each volumetric flask as in procedure for sample analysis (**9.3**). Read the absorbance of each standard against reagent blank.

10.2 Calibration Curve

Plot the absorbance as the ordinate versus the concentration as abscissa on linear graph paper.Alternatively, determine the slope by the method of least squares. Resultant 5-point calibration curve corresponds to 5, 10, 15, 20, 25 µg of ammonia/25 ml of solution.

10.3 Sample Analysis

Transfer only 10 ml of absorbing solution from impinger to a 25 ml capacity volumetric flask.Bring all solutions and sample at 25 °C $\pm$ 2 °C. Add 2 ml buffer and 5 ml of working phenol solution to the flask, mix and fill to about 22 ml. Then add 2.5 ml of the working hypochlorite solution and mix rapidly. Dilute to 25 ml, mix, and store in the dark at 25 °C for 30 min to develop color. Measure the absorbance of the solution against a reagent blank at 630 nm, using 1 cm cells.

11 CALCULATION

$$C \ (\mu g/m^3 \ NH_3) \ = \ \frac{W}{Vo} \times \frac{Volume \ of \ absorbing \ solution \ in \ impinger}{Aliquot \ taken \ for \ analysis}$$

$$C \ (\mu g/m^3 \ NH_3) \ = \ \frac{W}{Vo} \times \frac{25}{10}$$

where,

C = concentration of ammonia in µg/m^3;

W = µg NH$_3$ in 25 ml from standard curve; and

Vo = volume of air sample in m^3.

If values need to be reported after normalization, calculate volume using the following equation at 25 °C and 101.3KPa (760 mm Hg):

$$V_O \ = \ \left(\frac{F}{1000}\right) \times \left(\frac{P_S}{101.3}\right) \times \left(\frac{298}{273 + T_S}\right)$$

where,

F = Flow rate (l/min),

Ps = atmospheric pressure in kPa at sampling point, and

Ts = ambient temperature, °C at sampling point.

12 QUALITY ASSURANCE/QUALITY CONTROL MEASURES

12.1 Calibration

Periodic calibration of the gas sampler shall be performed as per the calibration plan preparedby laboratory at such intervals as determined based on use and subject to performance of intermediate checks at regular intervals for flow to maintain confidence in the performance ofsampler. The acceptance criteria for flow rate shall be $\pm$ 5 percent. Laboratory shall maintain a master calibrator for doing intermediate checks in-house.

12.2 Field Blank

Purpose of field blank is to detect and identify any contaminant from the sampling site including travelling to and from the laboratory to the site. For field blanks, impinger with absorbing solution is placed in the sampler for the sampling duration. The air is not bubbledthrough the impingers. By doing this, the field blanks are exposed to the atmosphere of the sampling site and any contamination due to handling. The absorbing solution is analyzed forany concentrations of interest.

12.3 Leak Check Procedure and Criteria

Follow the sampler manufacturer's manual to do the leak check (**7.1.1.4**) which must meetpredefined leak check acceptance criteria. Create 200 mmHg vacuum in the complete sampling system including inlet/outlet tubing with many fold, valves and impinger. Vacuum must notreduce more than 25 mmHg in 3 min.

12.4 Proficiency Testing

Laboratories shall participate in proficiency testing programs as per the Proficiency Testingplan prepared by laboratory.

ANNEX A

(Clause 2)

LIST OF REFERRED STANDARDS

IS No.	*Title*
IS 265: 2021	Hydrochloric acid specification (*fifth revision*)
IS 266: 2024	Sulphuric acid — Specification (*fourth revision*)
IS 376: 2023	Sodium hydroxide analytical reagent — Specification (*fourth revision*)
IS 538: 2000	Phenol (Carbolic Acid) — Specification (*third revision*)
IS 1070: 2023	Reagent Grade Water — Specification (*fourth revision*)
IS 2303 (Part 1/Sec 1): 2021/ISO 719: 2020	Grading glass for alkalinity Part 1 Hydrolytic resistance of glassgrains Section 1 Determination and classification of hydrolytic resistance at 98°C (*third revision*)
IS 4167: 2020	Glossary of terms relating to air pollution (*second revision*)
IS 5182 (Part 14): 2000	Methods for measurement of air pollution Part 14 Guidelines for planning the sampling of atmosphere
IS/ISO 17034: 2016	General requirements for the competence of reference material producers