

BUREAU OF INDIAN STANDARDS

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Draft Indian Standard

Ammonium Bifluoride — Specification

(First Revision of IS 13119)

भारतीय मानक मसौदा

अमोनियम बाइफ्लोराइड — विशिष्टि

(पहला पुनरीक्षण)

(ICS No. 71.060.50)

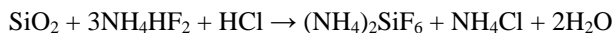
Water Quality for Industrial Purposes Sectional Committee,
CHD 13

Last Date of Comment: 18.05.2024

FOREWORD

(Formal clause to be added later)

Ammonium bifluoride is a constituent in chemical cleaning agents used for removal of siliceous scales in boiler tubes. For efficient working of boilers, the boiler tubes have to be descaled periodically. The scale consists mainly oxides of calcium, magnesium, iron and silica. The reaction of silica and ammonium bifluoride in the presence of hydrochloric acid is as follows:



Ammonium bifluoride converts the siliceous scale into water soluble compounds and thus eases the cleaning process. Besides, it also catalyses the reaction between the acid used in cleaning mixture and the metallic scales, such as mill scales, rust, etc.

Ammonium bifluoride also finds application in sugar industry as a bactericide; in breweries and distilleries as a disinfectant; in wood as preservative; in metal industry as pickling agents; in aluminium industry for anodizing; in glass and electric bulb industry for frosting, polishing and etching; in oil drilling for softening the siliceous rocks; in textile industry as a scouring agent and in nuclear engineering for the separation of uranium from iron, vanadium, beryllium and zirconium.

This Indian standard was first published in 1991. In this first revision the following changes have been incorporated

- a) Colorimetric method of determination has been incorporated as referred IS 4542 has been withdrawn; and
- b) Inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS) method for determination of heavy metals (as Pb) and iron have been incorporated; and
- c) The Packaging clause has been modified.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

1 SCOPE

This standard prescribes the requirements and methods of sampling and test for ammonium bifluoride.

2 REFERENCES

The standards given below contain provisions which through reference in this text, which constitute provisions of this standard. At the time of publications, 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 these standards given below:

<i>IS No.</i>	<i>Title</i>
IS 251: 1982	Soda ash, technical — Specification (<i>fourth revision</i>)
IS 1070: 2023	Reagent Grade Water Specification (<i>fourth revision</i>)
IS 3025	Methods of sampling and test (Physical and Chemical) for water and wastewater
(Part 2): 2019 ISO 11885 : 2007	Part 2 determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (<i>first revision</i>)
(Part 24)	Part 24 Sulphates
(Sec 1): 2022	Section 1 Gravimetric and Turbidity Methods (<i>second revision</i>)
(Sec 2): 2021 ISO 22743 : 2006	Section 2 Method by Continuous Flow Analysis
(Part 35): 1988	Part 35 silica (<i>first revision</i>)
(Part 47): 1994	Part 47 lead (<i>first revision</i>)
(Part 53) : 2003	Part 53 iron (<i>first revision</i>)
IS 4161: 2023	Nessler Cylinder — Specification (<i>first revision</i>)
IS 4905: 2015 ISO 24153 : 2009	Random sampling and randomization procedures (<i>first revision</i>)
IS 5762: 1970	Methods for determination of melting point and melting range
IS 11671: 2022	Glossary of terms relating to boiler water (<i>second revision</i>)

3 TERMINOLOGY

For the purpose of this standard, definitions given in IS 11671 shall apply.

4 REQUIREMENTS

4.1 Description

The material shall be in the form of white deliquescent crystalline solid.

4.2 The material shall also comply with the requirements as specified in Table 1.

Table 1 Requirements for Ammonium Bifluoride

(Clause 4.2, 7.1)

Sl. No.	Characteristic	Requirement	Method of Test, Ref to	
			Annex	IS No.
(1)	(2)	(3)	(4)	(5)
i)	Ammonium bifluoride content, percent by mass, <i>Min</i>	97.0	Annex A	-
ii)	Melting point, °C	126 to 126.2	-	IS 5762
iii)	Matter insoluble in water at 27 °C, <i>Max</i>	0.2	-	C-4 of IS 251
iv)	Silica [as (NH ₄) ₂ SiF ₆], percent by mass, <i>Max</i>	0.1	-	IS 3025 (Part 35)
v)	Sulphate [as (NH ₄) ₂ (SO ₄)], percent by mass, <i>Max</i>	0.4	-	IS 3025 (Part 24/Sec 1) or IS 3025 (Part 24/Sec 2)
vi)	Heavy metals (as Pb), percent by mass, <i>Max</i>	0.15	Annex B	-
vii)	Iron (as Fe), percent by mass, <i>Max</i>	0.1	Annex C	-

5 PACKING AND MARKING

5.1 Packing

The material shall be packed in laminated high-density polyethylene (HDPE) bags having inner liner and then the outer laminated HDPE woven sack shall be stitched using polypropylene or nylon thread with two rows – each row being done separately – one being above the other for the protection during transit. The material may also be packed in polyethylene containers, polyethylene lined steel drums or other containers as agreed to between the purchaser and the supplier.

5.2 Marking

5.2.1 The container shall bear legibly and indelibly the following information:

- Name of the material;
- Name of the manufacture and trade-mark, if any;
- Net mass of the material in package and tanker;
- Date of manufacture;
- Batch number/Lot number; and
- A cautionary notice worded as:

AMMONIUM BIFLUORIDE IS POISONOUS. EXTREME CARE AND APPROPRIATE MEASURE MUST BE TAKEN TO ENSURE THAT THIS POISONOUS PRODUCT IS NOT TAKEN BY MOUTH OR INHALED AS DUST. CONTACT WITH SKIN SHOULD BE AVOIDED BY WEARING NECESSARY PROTECTIVE EQUIPMENT LIKE PVC HAND GLOVES, APRON AND GOGGLES.

5.2.2 BIS Certification Marking

The product(s) conforming to the requirements of this standard may be certified as per the conformity assessment schemes under the provisions of the *Bureau of Indian Standards Act*, 2016 and the rules and regulations framed there under, and the products may be marked with the Standard Mark.

6 SAMPLING

6.1 General Requirements of Sampling

6.1.1 In drawing, preparing, storing and handling samples, the necessary precautions and directions shall be observed. Particular attention is drawn to the fact that ammonium bifluoride is poisonous and extreme care and precautionary measures are to be taken during sampling to ensure that the product is not taken by mouth or inhaled as dust. Further, contact with the skin should also be avoided.

6.1.2 Samples shall not be drawn in an exposed place.

6.1.3 The sampling instruments shall be clean and dry.

6.1.4 Precautions shall be taken to protect samples, the material being sampled, the sampling instruments and the containers for samples from adventitious contamination. To draw a representative sample, the contents of each container selected for sampling shall be mixed as thoroughly as possible by suitable means.

6.1.5 The samples shall be placed in clean and air-tight polyethylene bottles on which the material has no action and which have been previously washed several times with the material to be sampled.

6.1.6 The sample containers shall be of such a size that they are filled by the sample leaving an ullage of not more than five percent.

6.1.7 Each sample container shall be sealed airtight after filling, and marked with full details of sampling including the date of sampling and the year of manufacture of the material.

6.2 Scale of Sampling

6.2.1 Lot

All the containers or drums or bags in a single consignment of the material drawn from a single batch of manufacture shall constitute a lot. If a consignment is declared or known to consist of different batches of manufacture, the containers shall be grouped separately and those containers belonging to the same batch shall constitute a lot.

6.2.2 For ascertaining conformity of ammonium bifluoride to the requirements of this specification, samples shall be tested from each lot separately. The number of containers to be selected at random from the lot shall be in accordance with Table 2.

Table 2 Number of Containers to be Selected for Sampling

Sl. No.	Lot Size	Sample Size
(1)	(2)	(3)
i)	up to 50	3
ii)	51 to 100	4
iii)	101 and above	5

6.2.2.1 In order to ensure randomness of selection, guidance may be had from IS 4904.

6.3 Preparation of Test Samples

From each of the containers selected according to **6.2.2**, small portions of 25 g of the material shall be taken out and stored in individual sample containers. These individual samples shall then be mixed together to form a composite sample. This composite sample shall be divided into three parts, one for the purchaser, one for the supplier and finally one as referee sample. All the tests for the requirements given in this standard shall be carried out on the composite sample.

6.4 Criteria for Conformity

The lot shall be declared as conforming to the requirements of this specification if all the test results on the composite sample satisfy the corresponding requirements.

7 TESTS

7.1 Tests shall be carried out by the appropriate methods prescribed in **col 4** and **col 5** of Table 1.

7.2 Quality of Reagents

Unless specified otherwise, pure chemicals and distilled water (*see* IS 1070) shall be employed in tests.

NOTE — ‘Pure chemicals’ shall mean chemicals that do not contain impurities which affect the results of analysis.

ANNEX A
[Table 1, *SI No. (i)*]

DETERMINATION OF AMMONIUM BIFLUORIDE

A-1 GENERAL

Three methods, namely, titration with thorium nitrate (**A-2**), distillation method (**A-3**), and titration with sodium hydroxide (**A-4**), have been prescribed.

A-2 DETERMINATION OF TOTAL FLUORIDE BY TITRATION METHOD

A-2.1 Outline of the Method

Sample is dissolved in water, made to a volume and an aliquot is titrated with standard thorium nitrate solution using sodium alizarin sulphonate as indicator.

A-2.2 Reagents

A-2.2.1 Thorium Nitrate Solution, approximately 0.05 N

Dissolve 7.045 g of thorium nitrate tetrahydrate [$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$] in water and make up to 1 000 ml.

A-2.2.2 Buffer Solution

Dissolve 50 g of mono-chloroacetic acid in 250 ml of 1 N sodium hydroxide solution and dilute to 500 ml.

A-2.2.3 Dilute Hydrochloric Acid, approximately 0.1 N

A-2.2.4 Sodium Hydroxide Solution, 20 g/l

A-2.2.5 Sodium Alizarin Sulphonate Indicator Solution, 0.5 g/l

Dissolve 0.05 g of the indicator in water and dilute to 100 ml.

A-2.2.6 Sodium Fluoride Standard Solution

Dissolve 0.28 g of anhydrous sodium fluoride in distilled water and dilute to 500 ml in a volumetric flask. One millilitre of this solution will contain 0.253 mg of fluoride as F and call it as '*t*'. Calculate the factor '*f*' for 1 ml of thorium nitrate solution in terms of fluoride concentration as described in **A-2.2.7**.

A-2.2.7 Determination of Factor (*f*)

Transfer 25 ml of standard fluoride solution (**A-2.2.6**) into a 250 ml conical flask and titrate against thorium nitrate solution using sodium alizarin sulphonate solution as indicator by the method described in **A-2.3**

$$\text{Factor, } f = \frac{25 \times t}{A}$$

where

A = volume of thorium nitrate solution consumed in the titration, in ml.

A-2.3 Procedure

Weigh to the nearest 0.001 g about 0.25 g of finely powdered sample in a plastic weighing bottle and dissolve in a little quantity of water and transfer the sample solution quantitatively into a 500 ml volumetric flask. Dilute to the mark and mix. Transfer 50 ml aliquot of this solution into a 250 ml conical flask and add 1 ml of sodium alizarin sulphonate solution. Acidify the solution slightly by titration and back titrate with sodium hydroxide and hydrochloric acid solutions until the reddish tinge formed just disappears. Add 2 ml of buffer solution and titrate with the thorium

nitrate solution until a persistent pale pink colour is obtained. The colour becomes particularly noticeable when the precipitated mass is allowed to settle. Note the titre reading. Carry out a blank test with the same quantity of all the reagents but omitting the sample. Note the titre reading.

A-2.4 Calculation

A-2.4.1 Ammonium bifluoride (NH_4HF_2), percent by mass = $\frac{F \times 57}{38}$

where

F is calculated as explained in A-2.4.2.

A-2.4.2 Total fluoride (as F), percent by mass = $\frac{(V_1 - V_2) \times f}{M} \times 100$

where

V_1 = volume, in ml, of standard thorium nitrate solution used in titration of the test solution;

V_2 = volume, in ml, of standard thorium nitrate solution used in blank titration;

f = a factor equivalent to mass, in g, of fluoride as F corresponding to 1 ml of the standard thorium nitrate solution (A-2.2.7); and

M = mass, in g, of the test sample.

NOTE

If the percentage of ammonium bifluoride (NH_4HF_2) calculated as above exceeds 100, it indicates the presence of free hydrofluoric acid which is normally present in the material.

A-3 AMMONIA METHOD

A-3.1 Outline of the Method

The sample solution is distilled with strong sodium hydroxide solution and the ammonia quantitatively expelled is absorbed in excess of standard hydrochloric acid. Ammonia absorbed is determined by back titration of the excess of acid with standard sodium hydroxide solution.

A-3.2 Reagents

A-3.2.1 *Sodium Hydroxide Solution*, 10 percent (m/v)

A-3.2.2 *Standard Hydrochloric Acid Solution*, 0.5 N

A-3.2.3 *Standard Sodium Hydroxide Solution*, 0.5 N

A-3.2.4 *Methyl Red Indicator Solution*, 1 percent (m/v) in ethanol

A-3.3 Apparatus

The distillation apparatus may be as given in Fig. 1.

A-3.4 Procedure

A-3.4.1 Assemble the distillation apparatus as given in Fig. 1. 'A' is a 1 litre round bottom distillation flask with a two-holed rubber stopper having a tap funnel 'B' and a spray trap 'C'. Condensor 'D' is attached to the trap by means of a rubber bung and 'E' is a 250 ml conical flask.

A-3.4.2 Weigh accurately about 1.0 g of the test sample and dissolve in a little quantity of water and transfer this solution quantitatively into the distillation flask 'A'. Add about 200 ml of water and a few pieces of glass beads to the flask.

A-3.4.3 Place 50 ml of standard hydrochloric acid (A-3.2.2) and about 50 ml of water in the conical flask 'E'. Adjust the flask so that the end of the condenser just dips into the acid. Make sure that all the connections of the apparatus are air-tight.

A-3.4.4 Take 100 ml of 10 percent sodium hydroxide solution into the funnel 'B' and run the solution into the distillation flask by opening the tap 'F'. Close the tap immediately after transferring the sodium hydroxide solution.

A-3.4.5 Heat the flask to boil the contents gently and continue the distillation for 30 min to 40 min to distil all the ammonia into the receiver 'E'. Open the tap 'F' before removing the flame, disconnect the trap from the top of the condenser, lower the conical flask and rinse the condenser with little water.

A-3.4.6 Add a few drops of methyl red indicator and titrate the excess of acid with standard sodium hydroxide solution (A-3.2.3).

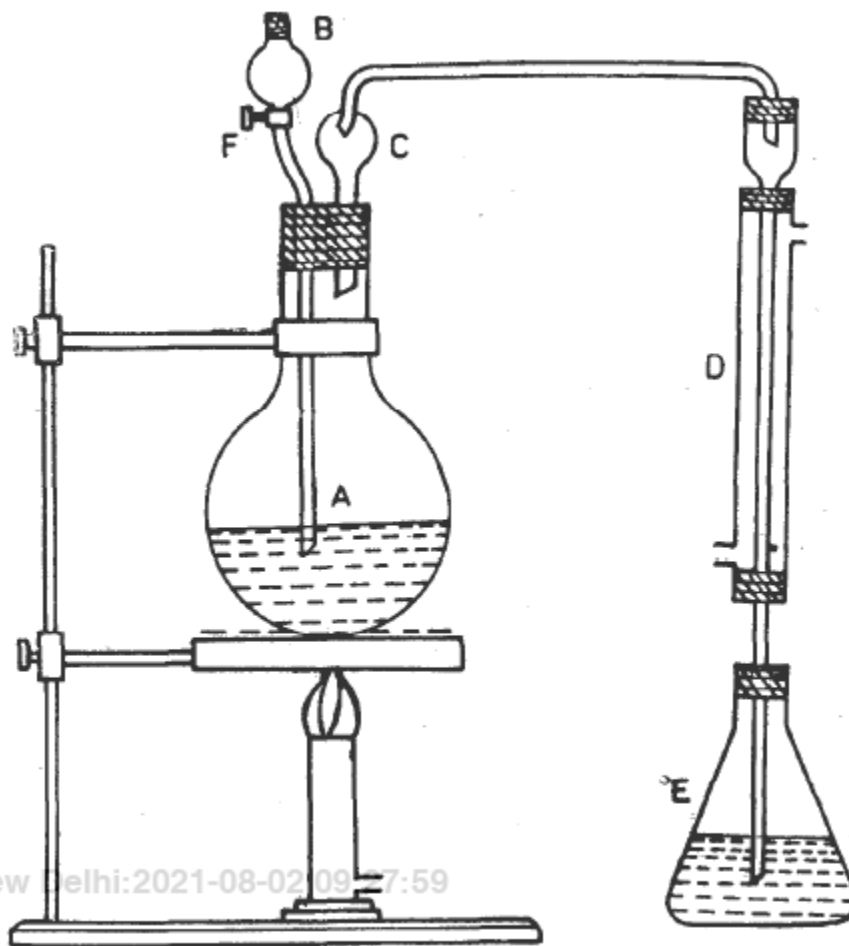


FIG. 1 APPARATUS FOR DETERMINATION FOR AMMONIA

A-3.5 Calculation

A-3.5.1 Ammonia (as NH_3), percent by mass, $A = \frac{(50-V) \times 0.85}{M}$

where

V = volume of 0.5 N standard sodium hydroxide solution used in back titration, in ml; and

M = mass of the test sample, in mg.

A-3.5.2 Ammonium bifluoride (NH_4HF_2), percent by mass = $\frac{A \times 57}{17}$

A-4 DETERMINATION OF AMMONIUM BIFLUOR (DE BY TITRATION METHOD

A-4.1 Outline of the Method

Sample is dissolved in water, made to a volume and an aliquot is titrated with standard sodium hydroxide solution using bromothymol blue indicator.

A-4.2 Reagents

A-4.2.1 *Standard Sodium Hydroxide Solution, 0.1 N*

A-4.2.2 *Bromothymol Blue Indicator Solution*

Triturate 0.10 g of bromothymol blue indicator powder of analytical grade in 8.0 ml of 0.02 N sodium hydroxide solution with 250 ml of distilled water.

A-4.3 Procedure

Weigh to the nearest 0.001 g about 1 g of finely powdered sample, dissolve in small volume of distilled water and transfer the sample solution quantitatively into a 100 ml HDPE volumetric flask. Transfer 20 ml aliquot of the solution into a clean 250 ml HDPE conical flask and add 1 ml of bromothymol blue indicator solution. Titrate with sodium hydroxide solution (**A-4.2.1**) until the colour changes from yellow to blue. Note the titre reading.

A-4.4 Calculation

$$\text{Ammonium bifluoride (NH}_4\text{HF}_2\text{), percent by mass} = \frac{V \times 5 \times 100 \times f}{17}$$

where

V = volume of standard sodium hydroxide solution used in titration of the test solution, in ml;

f = factor equivalent to mass, in g, ammonium bifluoride as (NH₄HF₂) corresponding to 1 ml of the 0.1 N standard sodium hydroxide solution — 0.005 704; and

M = mass of the test sample, in g.

ANNEX B

[Table 1, Sl No. (vi)]

DETERMINATION OF HEAVY METALS

B-1 OUTLINE OF THE METHOD

This method prescribes a calorimetric method for determination of heavy metals as lead using colour development by dithizone and comparing the colour against colour developed by standard lead solution. Alternatively lead to be determined by atomic absorption spectrophotometry as per IS 3025 (Part 47) (Referee method) and by inductively coupled plasma optical emission spectrometry (ICP-OES) as per IS 3025 (Part 2) (alternate method).

B-2 APPARATUS

B-2.1 *Nessler Cylinders, 50 ml capacity (see IS 4161).*

B-3 REAGENTS

B-3.1 Standard Lead Solution

Dissolve 0.40 g of lead nitrate [Pb(NO₃)₂] in water containing 2 ml or 3 ml of concentrated nitric acid and make up the volume to 1 litre with water. Transfer 10 ml of this solution to a 1 ml volumetric flask, add 2 ml or 3 ml of concentrated nitric acid and dilute with water to 1 litre [1 ml = 2.5 µg of lead (as Pb)]. The dilute solution shall be prepared fresh.

B-3.2 *Dilute Ammonium Hydroxide Solution, 1 N, approximately*

B-3.3 Reagent A

Dissolve 25 g of tri-ammonium citrate or 22 g of citric acid and 4 g of hydroxylamine hydrochloride in about 200 ml of water. Add dilute ammonium hydroxide to bring the pH to 8.5. Dilute the solution to 500 ml. Purify this solution by extracting with 1.5 ml portions of 0.01 percent dithizone solution until the final colour of the dithizone extract is green. Wash the aqueous remainder portion three times with 25 ml portions of chloroform and finally with one 25 ml portion of carbon tetrachloride.

B-3.4 Dithizone (Diphenyl Thiocarbazon or Phenyl-azothionoformic Acid) Solution

Dissolve 0.01 g of dithizone in 100 ml of carbon tetrachloride, shaking intermittently for 1 h. Allow to stand overnight and shake once again before using. This shall be kept in a cool and dark place. This contains 0.01 percent solution. Filter, if necessary. Dilute 10 ml of this solution to 100 ml with carbon tetrachloride in a 100 ml volumetric flask. This shall be prepared fresh before determination. This gives a solution of 0.001 percent.

NOTES

1 Carbon tetrachloride used should be further purified. One litre of carbon tetrachloride is extracted with two portions of 25 ml of dilute ammonium hydroxide and then kept over 100 g of activated carbon. Before use, it is decanted and distilled at about 80 °C over a little fresh lime.

2 Sometimes dithizone solid and its 0.01 percent solutions deteriorate on storage. The 0.1 percent solution should, therefore, be tested before further dilution, by shaking 2 ml of the solution with 5 ml of 1 percent ammonium hydroxide. If the organic layer is only faintly yellow under these conditions, the solution may be used. If it is deeply coloured, it shall be discarded and fresh solution prepared. The solution as well as the reagent should be stored in a refrigerator and exposure to sunlight should be avoided during analytical work. To increase the stability of 0.01 percent solution, it should be covered with a thin aqueous layer saturated with sulphur dioxide.

B-3.5 Thymol Blue Indicator Solution

1 percent (m/v) solution in rectified spirit.

B-4 PROCEDURE

B-4.1 Take several aliquots of standard lead solution into a series of separating funnels, add 5 ml of water and 10 ml of the Reagent A. Then add 2 drops of thymol blue indicator and bring the pH of the solution to 8.5 by adding dilute ammonium hydroxide. Add 5 ml of the dithizone solution and shake well for about 10 sec. Drain the organic layers into stoppered Nessler cylinders.

B-4.1.1 Dissolve about 10 g of material accurately weighed, in a 100 ml volumetric flask. Take a suitable aliquot of the solution, and transfer to a separating funnel. Develop the colour as prescribed in **B-4.1**. Drain the organic layer into a stoppered Nessler cylinder, add 10 ml of dilute ammonium hydroxide, and shake for about 10 sec. Compare the colour developed with those of the standard solutions. Note the volume of the standard with which the colour of the test solution matches.

NOTE

If the colour of the test solution is intermediate between two standard solutions, then the experiment is repeated by taking more number of standard solutions in that range and exact colour matching is arrived at.

B-5 CALCULATION

B-4.1 Heavy metals (as Pb), percent by mass = $\frac{100 \times V \times f}{M}$

where

V = volume of standard lead solution matching with the test solution, in ml;

f = mass of heavy metals (as Pb) equivalent to 1 ml of standard lead solution (**B-3.1**), in g; and

M = mass of the material in the aliquot taken for test, in g.

B-5 REFEREE METHOD

Determine lead content by Atomic Absorption Spectrophotometer as per method given in IS 3025 (Part 47).

B-6 ALTERNATE METHOD

Determine lead content by ICP-AES as prescribed in IS 3025 (Part 2).

ANNEX C
[Table 1, Sl No. (vii)]

DETERMINATION OF IRON

C-1 PRINCIPLE

Iron (III) reacts with thiocyanate to give a series of internally red coloured compounds, which remains in true solution. Strong acids (hydrochloric acid) should be present to compress the hydrolysis. Alternatively iron to be determined by atomic absorption spectrophotometry as given in IS 3025 (Part 53) (referee method) & ICP-OES (Alternate method)

C-2 APPARATUS

C-2.1 Nessler Cylinders, 100 ml capacity

C-3 REAGENTS

C-3.1 Dilute Hydrochloric Acid, approx. 4 N

C-3.2 Ammonium Persulphate (Solid)

C-3.3 Ammonium Thiocyanate Solution

Dissolve 10 g of ammonium thiocyanate in 100 ml distilled water.

C-3.4 Standard Iron Solution A

Dissolve 0.7022 g of ferrous ammonium sulphate $[\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ in water in a 1 000 ml volumetric flask, add 4 ml of concentrated sulphuric acid and make up to the mark with water. One milliliter of this solution contains 0.1 mg of Iron (as Fe).

C-3.5 Standard Iron Solution B

Take 100 ml of standard iron solution A (*see C-3.4*), add dilute potassium permanganate solution (0.2 percent, *m/v*) drop wise with constant stirring, until a slight pink colour persists after stirring and dilute to the mark in a 1 000 ml volumetric flask. This dilute solution should be prepared afresh. One milliliter of this solution contains 0.01 mg of Iron (as Fe).

C-4 PROCEDURE

Dissolve 1g of the accurately weighed material in 10 ml of water contained in a Nessler cylinder. Add 2 ml of dilute hydrochloric acid and dilute to about 45 ml. Add about 30 mg of Ammonium persulphate and 3 ml of Ammonium Thiocyanate solution. Dilute to 100 ml mark and mix. Carry out a control test in another Nessler cylinder using distilled water. Using a micro pipette, add standard iron solution B (*see C-3.5*) to the blank and shake well, until the colour matches to that of a sample.

C-5 CALCULATION

$$\text{Iron content as Fe, percent by mass} = \frac{V \times 0.001}{M}$$

where

V = Volume of standard iron solution (B), in ml; and

M = Mass of sample taken for the test, in g.

C-6 REFEREE METHOD

Determine iron content by atomic absorption spectrophotometry method as given in IS 3025 (Part 53).

C-7 ALTERNATE METHOD

Determine iron content by ICP-OES as prescribed in IS 3025 (Part 2).