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*Draft Indian Standard*

**Specification for Feed Water, Boiler Water, and Condensate Water for High Pressure Boilers**  
(First Revision of IS 10496)

भारतीय मानक मसौदा  
उच्च दबाव बॉयलरों के लिए फ़ीड जल, बॉयलर जल और कंडेनसेट जल के लिए विशिष्टि  
(पहला पुनरीक्षण)

(ICS No. 27.060.30, 13.060.50)

Water Quality for Industrial Purposes Sectional  
Committee, CHD 13

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**FOREWORD**

**(Formal clause to be added later)**

The chief object of treatment of water for boilers is to minimize corrosion and to prevent formation of scale in water – steam circuit of the boiler. The chemical methods of attaining the desirable conditions in the water side of boilers operating above 5.9 MN/m<sup>2</sup> (60 Kgf/cm<sup>2</sup>) are given in IS 4343: 2023.

This standard was first published in 1983. In this first revision the following modifications have been incorporated:

- Specification of feed water, boiler water, and condensate have been revised in light of the latest technological developments;
- Requirement for feed water through once-through boilers have been deleted as Technical Committee responsible for formulation of standard IS 10496 has decided to formulate a separate standard on water quality for once through boilers;
- Method of test for morpholine, cyclohexylamine, and nickel have been removed;
- References, ICS No. have been updated; and
- Other editorial changes have been done to bring the standard in the latest style and format of Indian Standards.

In the preparation of this standard, considerable assistance has been drawn from BS EN 12952-12: 2003 Water-tube boilers and auxiliary installations Part 12: Requirements for boiler feed water and boiler water quality and VGB –standard (VGB-S-010-T-00) 2011-12 EN, Feed water, Boiler water and Steam Quality for Power Plants.

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 (*second revision*).

## 1 SCOPE

**1.1** This standard prescribes requirements for feed water, boiler water, steam and condensate for water-tube boilers.

**1.2** The requirements prescribed are for boilers operating at pressures above 5.9 MN/m<sup>2</sup> (60 kg/cm<sup>2</sup>) during normal operation of the unit with normal water level in boiler and with nominal output at nominal pressure. Any serious deviation from the above shall be discussed in advance with the boiler manufacturer.

## 2 REFERENCES

The standards listed below 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.

<i>IS No.</i>	<i>Title</i>
IS 3025 (Part 11): 2022	Methods of sampling and test (Physical and Chemical) for water and waste water: Part 11 pH value ( <i>second revision</i> )
IS 3025 (Part 14): 2013	Methods of sampling and test ( physical and chemical) for water and wastewater: Part 14 Specific conductance (wheatstone bridge, conductance cell ) ( <i>second revision</i> )
IS 3025 (Part 21) : 2009	Methods of sampling and test (Physical And Chemical) for water and wastewater: Part 21 hardness ( <i>second revision</i> )
IS 3025 (Part 31/Sec 1) : 2022	Methods of sampling and test (physical and chemical) for water and wastewater: Part 31 PHOSPHORUS; Section 1 Determination by Vanadomolybdo-phosphoric acid Stannous chloride Ascorbic acid and Persulphate method ( <i>second revision</i> ).
IS 3025 (Part 35): 1988	Methods of sampling and test (physical and chemical ) for water and wastewater : Part 35 Silica ( <i>first revision</i> )
IS 3025 (Part 38) : 1989	Water and wastewater - Methods of sampling and test (Physical and Chemical): Part 38 dissolved oxygen ( <i>first revision</i> )
IS 3025 (Part 42) : 1992	Methods of sampling and test (Physical and Chemical) for water and wastewater: Part 42 copper ( <i>first revision</i> )
IS 3025 (Part 45) : 1993	Methods of sampling and test (Physical and Chemical) for water and wastewater: Part 45 sodium and potassium ( <i>first revision</i> )

IS 3025 (Part 53) : 2003	Methods of sampling and test (Physical and Chemical) for water and wastewater: Part 53 iron ( <i>first revision</i> )
IS 3025 (Part 73) : 2021 ISO 20236 : 2018	Methods Of Sampling And Test Physical And Chemical For Water And Wastewater: Part 73 Instrument based method for determination of total organic carbon TOC dissolved organic carbon DOC total bound nitrogen TNb and dissolved bound nitrogen DNb
IS 17614 (Part 1) : 2021 ISO 5667-1 : 2020	WATER QUALITY – SAMPLING: Part 1 Guidance on the design of sampling programmes and sampling techniques
IS 17614 (Part 3) : 2021 ISO 5667-3 : 2018	WATER QUALITY – SAMPLING: Part 3 Preservation and handling of water samples

### 3 REQUIREMENTS

#### 3.1 Water-Tube Boilers (Drum Type)

The feed water, boiler water, steam and condensate, for water-tube boilers shall comply with the requirements as specified in Table 1 to Table 4.

NOTE — In case of recovery boilers operating at low boiler pressures of 1.5 MN/m<sup>2</sup> to 2.0 MN/m<sup>2</sup> and above, the boiler feed water used should be completely demineralized and the characteristics of the boiler feed water and boiler drum water should also be maintained as stringent as for high pressure boilers operated at 5.9 MN/m<sup>2</sup> pressure and above, since recovery boilers cannot tolerate even a minor tube leak while in operation due to poor and defective water treatment or conditioning which may lead to disastrous boiler explosions.

##### 3.1.1 Recommendation for Application of Requirements as Specified in Table 1 to Table 4

3.1.1.1 While applying the requirement as specified in Table 1 to Table 4 the following additional factors should also be kept in view.

###### 3.1.1.1.1 pH value of feed water

With cuprous feed heaters the range of pH values should be limited to 8.8 to 9.3 and without cuprous feed heaters to 9.2 to 9.6. For spray attemperation, the feed water should be dosed only with volatile chemical. For achieving feed water pH chemicals such as ammonia, cyclohexylamine, morpholine can be dosed at boiler feed pump suction.

###### 3.1.1.1.2 Oxygen

3.1.1.1.2.1 The oxygen limits as specified in Table 1 are those obtained after physical deaeration. In addition to physical deaeration, the use of a chemical oxygen scavenger is recommended. Hydrazine can be dosed at boiler feed pump suction /condensate extraction pump discharge.

3.1.1.1.2.2 Sodium sulphite should not be used in boilers operating above 5.9 MN/m<sup>2</sup> (60 kg/cm<sup>2</sup>) except where hydrazine cannot be used and then only if strict control is maintained to prevent damage due to its breaking down.

**3.1.1.1.2.3** Sodium sulphite should not be added to water used for spray attemperation.

**3.1.1.1.2.4** For low pressure plant, hydrazine is recommended as an alternative to sodium sulphite only when it is dosed to the feed water at a substantial distance from the boiler and where the feed water is sufficiently hot to enable the reaction with oxygen to be 90 percent complete before entry to the boiler. Thus, for smaller industrial plants, sodium sulphite would generally be preferred.

CAUTION - Hydrazine is toxic and suitable precautions for its handling should be observed. Its use is usually prohibited in hospitals, the food manufacturing industry and where the steam may come into contact with food or beverages.

**Table1 Requirements on Feed water for boilers with drum pressure > 60 kgf/cm<sup>2</sup>**

*(Clauses 3.1, 3.1.1, 3.1.1.1.2.1)*

S No.	Characteristics	Requirements	Methods of test reference	
			Annex	IS
(1)	(2)	(3)	(4)	(5)
i)	pH at 25 °C ( for copper alloy pre-boiler system)	8.8 - 9.3	—	IS 3025 (Part 11)/ISO 10523
ii)	pH at 25 °C (for all ferrous pre-boiler system)	9.2-9.6	—	IS 3025 (Part 11)/ISO 10523
iii)	Cation Conductivity at 25 °C, micro siemens/cm, <i>Max</i>	0.2	—	IS 3025 (Part 14)
iv)	Dissolved oxygen, ppm, <i>Max</i>	0.01	—	IS 3025 (Part 38) or IS 3025 (Part 38/Sec 2)
v)	Silica (as SiO <sub>2</sub> ), ppm, <i>Max</i>	0.02	A-3	IS 3025 (Part 35)
vi)	Iron (as Fe), ppm	0.01	A-1	IS 3025 (Part 53)

	a) For units without CPU, <i>Max</i>  b) For units with CPU, <i>Max</i>	0.005		
vii)	Copper (as Cu), ppm, <i>Max</i>  (mixed metallurgy units- AVT-R regime)	0.005	A-2	IS 3025 (Part 42)
viii)	Residual hydrazine, ppm	0.01-0.02	A-5	
ix)	Total organic carbon , ppm, <i>Max</i>	0.20	—	IS 3025 (Part 73)/ISO 20236
x	Total hardness	—	—	IS 3025 (Part 21)

NOTES

1 The concentration of the chemical parameter as per s no. iii), v), vi), and vii) in feed water cannot exceed the maximum concentration allowed in steam.

2 No copper monitoring is necessary if the steam – water cycle is free of copper alloys.

3 For copper alloy pre-boiler system, Dissolved oxygen in feed water less than 0.005 ppm is to be targeted with oxygen scavenger ( All volatile treatment – Reducing (AVT-R) ).

4 For all ferrous metallurgy pre-boiler system, oxygen scavenger is not needed if the dissolved oxygen after deaerator is less than 10 ppb. All Volatile Treatment with oxidizing (AVT – O) is recommended.

5 Considering the long term integrity of the plant, it is very essential to deliver the make-up water quality having lower limits than the concentration of the chemical species as per S No. iii), v), vi), vii), and x) under feed water.

6 For S No. iii), and iv) on-line measurement is recommended.

**Table 2 Requirements on boiler water for boilers with drum pressure > 60 Kgf/cm<sup>2</sup>***(Clauses 3.1, and 3.1.1)*

S No.	Characteristics	Requirements Drum pressure in Kgf/cm <sup>2</sup>		Methods of test reference	
		61 to 120	Above 120	Annex	IS
(1)	(2)	(3)	(4)	(5)	(6)
i)	pH at 25 °C	9.2-9.6	9.2-9.6	—	IS 3025 (Part 11)/ISO 10523
ii)	Specific conductivity at 25 °C, microsiemens/cm, <i>Max</i>	30	20	—	IS 3025 (Part 14)
iii)	Phosphate (as PO <sub>4</sub> ), ppm	0.2-4.0 <sup>1)</sup>	0.2-2.0 <sup>2)</sup>	—	IS 3025 (Part 31/Sec 1)
iv)	Silica ( as SiO <sub>2</sub> ), <i>Max</i>	20 <sup>3)</sup>		—	IS 3025 (Part 35)

## NOTES

1 In case of condensate leakage, at drum pressure 61 Kgf/cm<sup>2</sup> to 120 Kgf/cm<sup>2</sup> the phosphate requirement may go to 6 ppm.

2 In case of condensate leakage, at drum pressure 121 Kgf/cm<sup>2</sup> the phosphate requirement may go to 3.0 ppm.

3 For silica in main stream restrict to value of 20 ppb as given in Fig 1.

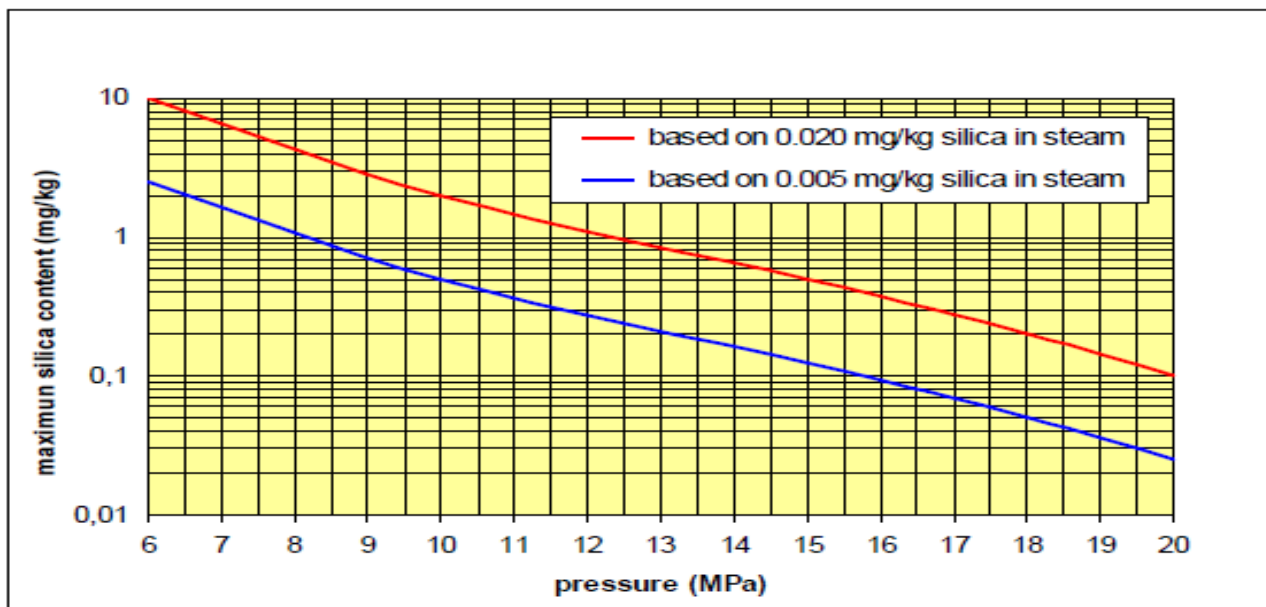


FIG 1 DRUM BOILER WATER SILICA CONTENT VERSUS PRESSURE TO ACHIEVE LESS THAN 20 PPB IN STEAM

**Table 3 Requirements on condensate for boilers with drum pressure > 60 Kgf/cm<sup>2</sup>**

(Clauses 3.1, and 3.1.1)

S No.	Parameter	Limits	Methods of test reference
(1)	(2)	(3)	(4)
i)	Cation Conductivity at 25 °C, micro siemens/cm, <i>Max</i>	0.20 ( <i>see Note</i> )	IS 3025 (Part 14)
ii)	Dissolved oxygen, ppb, <i>Max</i>	20 ( <i>see Note</i> )	IS 3025 (Part 38) or IS 3025 (Part 38/Sec 2)

**NOTE** — For S No. i), and ii) on-line measurement is recommended.

**Table 4 Requirements on steam for boilers with drum pressure > 60 Kgf/cm<sup>2</sup>**  
*(Clauses 3.1, and 3.1.1)*

S No.	Characteristics	Requirements	Methods of test reference	
			Annex	IS
(1)	(2)	(3)	(4)	(5)
i)	Cation Conductivity at 25 °C, micro siemens/cm, <i>Max</i>	0.20 ( <i>see Note</i> )	—	IS 3025 (Part 14)
ii)	Sodium, ppb, <i>Max</i>	5 ( <i>see Note</i> )	A-4	IS 3025 (Part 45)
iii)	Silica, ppb, <i>Max</i>	20 ( <i>see Note</i> )	A-3	IS 3025 (Part 35)

**NOTE** — For S No. i), ii), and iii) on-line measurement is recommended.

#### **3.1.1.1.3 Iron and copper**

The maxima for the sum of these impurities should be regarded as concentrations not to be exceeded, during continuous running conditions.

#### **3.1.1.1.4 Silica in feed water**

The concentrations of silica should not require blow down of boiler water in quantities exceeding the design value or exceeding the feed pump capacity. Where spray attemperation is employed, the spray water should contain as little silica as possible. When steaming a turbine, the spray water should contain less than 0.02 mg/l silica.

#### **3.1.1.1.5 Silica in boiler water**

Lower concentrations of silica may be advisable for steam for turbines which generally require less than 0.02 mg/l silica in steam. These values should also be employed for all boilers operating above 7.8 MN/m<sup>2</sup> (80 kg/cm<sup>2</sup>).

**NOTE** - For water tube boilers fitted with steam separating equipment, the maximum total solids content in steam should be 1 mg/l. It is generally accepted that steam should contain less than 0.02



mg/l of silica. In modern practice, sophisticated instruments like sodium analysers are used to determine the steam purity. The common guarantee of sodium in steam is less than 0.03 mg/l which corresponds to about 0.1 mg/l of total solids in steam.

#### **4 SAMPLING**

**4.1** Representative samples of feed water, boiler water and condensate shall be obtained as directed in IS 17614 (Part 1) and IS 17614 (Part 3). In particular, the following directions shall be observed.

**4.1.1** It is essential that a stainless steel or a monel metal cooler coil is fitted on the sampling cock so that the temperature of the water sample will be well below the boiling point at atmospheric pressure and there is no risk of aeration and concentration due to flashing into steam.

**4.1.2** Samples of feed water shall be obtained from the discharge of feed pump; samples of holler water from the top drum; samples of condensate from the discharge of the condensate extraction pump; and samples of make-up water from the evaporator stream range. All the above samples shall be obtained through a cooling coil as stated in **4.1.1** and collected in plastic or polyvinyl chloride bottles and stoppered immediately.

### **ANNEX A**

*(Table 1, Table 2, Table 3, and Table 4)*

#### **A-1 DETERMINATION OF IRON (PHOTOMETRIC BATHOPHENANTHROLINE METHOD)**

##### **A-1.1 Outline of the Method**

Total iron is determined by this method. Undissolved iron and iron oxides are put into solution by treatment with acid. The iron is reduced with hydroxylamine hydrochloride and then reacted with 4, 7 diphenyl-1, 10-phenanthroline (bathophenanthroline). The red ferrous complex is extracted from the aqueous solution with n-hexyl or isoamyl alcohol and the intensity of its colour is measured maximum absorption of the complex occurs at 533 nm, and Beer's law is valid.

**A-1.2 Interferences** - If the pH is between 3.3 and 3.7 a 1 mg/l ( ppm ) concentration of copper manganese, aluminium, zinc, magnesium, sodium, silica, nitrate, and orthophosphate ions does not interfere with the test.

##### **A-1.3 Apparatus**

###### **A-1.3.1 Nessler Tubes or Photometer**

Nessler tubes shall be 50 ml capacity.

NOTE — Contamination from unclean sample containers and laboratory glassware is a great source of error in this test. Soak all new glassware (for both sampling and testing) in hot hydrochloric acid (1+1) for 2 h. Drain and rinse at least 5 times with iron free-water. Before use, and after use (before again using), clean all glassware by making and iron extraction in each piece

(without separating the alcohol water layers). Drain and flush with iron-free methyl alcohol, ethyl alcohol, or isopropyl alcohol.

#### **A-1.4 Reagents**

**A-1.4.1** *Alcohol, n-Hexyl (preferred) or Isoamyl (alternative)*

**A-1.4.2** *Alcohol, Methyl, Ethyl, or Isopropyl*

**A-1.4.3** *Ammonium Hydroxide ( 1 + 1 )*

**A-1.4.4** *Bathophenanthroline Solution (0.835 g/litre)*

Dissolve 0.835 g of 4,7-diphenyl 1, 10-phenanthroline in 100 ml of ethyl alcohol (95 percent).

**A-1.4.5** *Hydrochloric Acid (HCl) (1 + 1)*

Cautiously add 500 ml of HCl (specific gravity 1.19) to 500 ml of water and mix. If iron content is high causing a high blank, distil in an all-glass apparatus, rejecting the first 50 ml and the last 100 ml of distillate.

**A-1.4.6** *Hydroxylamine Hydrochloride Solution (100 g/l)*

Dissolve 10 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in water and dilute to 100 ml. Purify as follows:

Adjust pH to 3.5 using a pH meter by drop wise additions of ammonium hydroxide (1 + 1) and hydrochloric acid (1 + 9). Transfer to separatory funnel, add 6 ml of bathophenanthroline solution and shake. Let stand for 1 minute. Add 20 ml of n-hexyl or isoamyl alcohol and shake for 1 minute. Let separate, remove aqueous layer, and discard alcoholic layer. Repeat extraction by again adding 3 ml of bathophenanthroline solution and 20 ml of alcohol with mixing. Discard the alcohol. If no further extractions are indicated make an extraction with alcohol alone and let settle a long enough time to remove all the alcohol layer. Discard the alcohol layer.

**A-1.4.7** *Iron, Standard Solution (1 ml = 1  $\mu\text{g}$  Iron as Fe)*

Pipette 10 ml of standard solution (1 ml = 0.1 mg iron as Fe) into a 1 litre flask, add 12 ml hydrochloric acid (1 + 1) and dilute to 1 litre with iron-free water. Prepare the dilute solution fresh before use.

#### **A-1.5 Calibration**

**A-1.5.1** Prepare a series of standards to cover the expected range of iron concentrations by diluting appropriate volumes of iron solution (*see A-1.4.7*). A standard calibration range from 20  $\mu\text{g/litre}$  to 80  $\mu\text{g/litre}$  produces excellent linearity.

**A-1.5.2** Transfer the iron standard to 125 ml separatory funnels. Dilute each to a volume of 50 ml with water. Add 2.0 ml hydroxylamine hydrochloride solution and mix. Add 3.0 ml of bathophenanthroline solution and shake for 30 s. Add ammonium hydroxide (1 + 1) drop wise with mixing until a distinct turbidity forms. Add hydrochloric acid (1 + 9) dropwise with mixing

until 1 drop clears the solution. The pH will be 3.5. Let stand for 1 min, then extract and proceed as described in **A-1.6.3** and **A-1.6.4**.

**A-1.5.3** Simultaneously carry out a blank determination containing no added iron using 50 ml of water and all reagents. Correct the readings of the standards for this blank value. For photometer comparisons, prepare a calibration curve by plotting the absorbance of the standards against the iron content in milligrams.

### **A-1.6 Procedure**

**A-1.6.1** Transfer a volume of sample containing no more than 8 µg of iron (*see* Note) to a beaker. If necessary, dilute to 50 ml with water and add 4 ml of hydrochloric acid (1 + 1). Add 2 ml of hydroxylamine hydrochloride solution and heat for 1 h at 60 °C. Cool to room temperature. Some samples may require other techniques for solubilizing the total iron.

NOTE — A 50 ml sample is ordinarily used. Depending upon the equipment used in colour measurement and the iron content, other volumes of sample may be used and adjusted to 50 ml.

**A-1.6.2** Transfer the sample to a 125-ml separatory funnel (*see* Note). Add 1 ml of hydroxylamine hydrochloride, then 3.0 ml of bathophenanthroline solution, and shake for 30 s. Add ammonium hydrochloride (1 + 1) drop wise with mixing until a distinct turbidity forms. Add hydrochloric acid (1 + 9) drop wise with mixing until 1 drop clears the solution. Let stand for 1 minute.

NOTE - Use either silicone stopcock grease on the stopcock or a funnel with TFE-fluorocarbon stopcock.

**A-1.6.3** Add 15.0 ml of n-hexyl or isoamyl alcohol and shake vigorously for 1 minute. Allow at least 15 minutes for complete separation of the water and alcohol layers; then drain the water layer from the funnel and discard. Shake out of the stem as much water as practical, then drain the alcohol layer into a 25 ml volumetric flask. Add 5 ml of methyl, ethyl, or isopropyl alcohol to the funnel and wash the internal surfaces by rolling and tumbling the funnel. Drain this alcohol into the previously drained alcohol extract. Dilute to the 25 ml mark with additional methyl, ethyl, or isopropyl alcohol and mix.

**A-1.6.4** Measure the colour of the alcohol solution. When using Nessler tubes, dilute the solution to the mark with more alcohol and mix. When using a photometer, adjust the instrument to zero absorbance reading with a reference solution consisting of the same alcohol mixture as used for the extraction of the colour.

**A-1.6.5** Carry out a blank determination on 50 ml of water with all reagents heating and extracting, in the same manner as for the sample. Correct the reading on the sample for this blank.

### **A-1.7 Calculation**

**A-1.7.1** Calculate the concentration of iron, in micrograms per litre, as follows:

$$\text{Iron, } \mu\text{g/litre} = (M \times 1000000)/S$$

where

M = mass of iron read iron calibration curve or present in matching standard in Nessler tube in mg; and  
S = volume of original sample used, in ml.

### **A-1.8 Range**

This method is specifically applicable to the determination of low concentrations of total iron (200 µg/l and below) in water.

## **A-2 DETERMINATION OF COPPER (NEOCUPROINE METHOD )**

### **A-2.1 Outline of the Method**

**A-2.1.1** In this method a choice between chloroform and isoamyl alcohol is given as the organic solvent used for extraction. The maximum absorption occurs at 457 nm when chloroform is used and at 453 nm when isoamyl alcohol is used.

**A-2.2 Interferences-** None of the ions commonly found in low-solids industrial water interferes with the test.

### **A-2.3 Apparatus**

#### **A-2.3.1 Nessler Tubes or Photometer**

A set of matched 50 ml Nessler tubes or a photometer may be used for evaluating the intensity of the colour produced.

### **A-2.4 Reagents**

#### **A-2.4.1 Chloroform Solvent**

Mix 9 volumes of chloroform ( $\text{CHCl}_3$ )1 with 1 volume of isopropyl alcohol).

#### **A-2.4.2 Copper Standard Solution** (1 ml = 4µg copper as Cu)

Dilute 200 ml of copper solution (1 ml = 0.02 mg Cu) to 1 litre with water.

#### **A-2.4.3 Hydrochloric Acid** (specific gravity 1.191 ), Concentrated hydrochloric acid.

#### **A-2.4.4 Hydroxylamine Hydrochloride Solution**, 200 g/l

Remove traces of copper from the solution by treating in a separatory funnel with neocuproine solution and chloroform solvent in accordance with **A-2.6.1** and **A-2.6.2**. Discard the organic extract.

#### **A-2.4.5 Isoamyl Alcohol**, copper-free.

#### **A-2.4.6 Isopropyl Alcohol**, copper-free.

#### **A-2.4.7 Neocuproine Solution**, 1 g/l

#### **A-2.4.8 Sodium Acetate Solution**, 275 g/l

Dissolve 55 g of sodium acetate trihydrate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ) in water and dilute to 200 ml. Remove traces of copper from the solution by treating in a Separatory funnel with hydroxylamine hydrochloride, neocuproine and chloroform solvent solution in accordance with **A-2.6.1** and **A-2.6.2**. Discard the organic extract.

### **A-2.5 Calibration and Standardization**

**A-2.5.1** Prepare a series of standard copper solutions for the measuring apparatus to be used. Prepare the standards in 250 ml Squibb separatory funnels by adding 0.4 ml of hydrochloric acid to suitable volumes of the standard copper solution ( $1 \text{ ml} = 4 \mu\text{g Cu}$ ) and diluting each to 200 ml with water. Also include a zero standard (blank) in the series by diluting 0.4 ml of the acid to 200 ml.

**A-2.5.2** If the copper content is to be determined by visual comparisons in Nessler tubes, proceed in accordance with **A-2.6.1** and **A-2.6.2** and then transfer each organic extract to a Nessler tube and dilute to the 50 ml graduation mark with isopropyl alcohol.

**A-2.5.3** If the copper content is to be determined by means of a photometer, proceed in accordance with **A-2.6.1** and **A-2.6.2** and measure the colour of the organic liquid obtained from each treated standard solution. For the initial photometer setting, use the organic liquid from the blank determination as a reference solution. Prepare a calibration curve, plotting the results on semilog graph paper. Plot percentage transmittance along the vertical single cycle log axis and the mass of copper (in  $\mu\text{g}$ ) along the horizontal linear axis. If the scale of the photometer reads directly in absorbance, use ordinary graph for plotting absorbance versus mass of copper (in  $\mu\text{g}$ ).

### **A-2.6 Procedure**

**A-2.6.1** Transfer 200 ml of well-shaken acidified, and unfiltered sample (for total copper) or 200 ml of filtered and acidified sample (for dissolved copper) into a 250 ml separatory funnel (*see* Notes 1 and 3) Maintain samples at a temperature of  $20 \text{ }^\circ\text{C}$  to  $30 \text{ }^\circ\text{C}$ . Add 1 ml of hydroxylamine hydrochloride solution and mix by shaking. Next, add 10 ml of sodium acetate solution and again shake. Then add 2 ml to 4 ml of neocuproine solution (*see* Note 4) and shake the funnel and contents for 1 min.

### NOTES

1 Separatory funnels with TFE-Tetra-fluoro Ethane stopcock are preferred. Use silicone grease to lubricate glass stopcock, but use only minimum amount needed.

2 In most cases, precipitated copper is readily dissolved by addition of acid to the sample To ensure complete dissolution it may be desirable in some instances to heat the acidified sample in the polyethylene bottle in which it was collected to  $70 \text{ }^\circ\text{C}$  to  $80 \text{ }^\circ\text{C}$  for 1 h by immersing the bottle-up to the neck in hot water sample in a beaker to minimize possible contamination. Avoid heating the sample in a beaker to minimize possible contamination.

3 If the sample contains more than the maximum concentration of copper for the applicable apparatus, a smaller size sample diluted to 200 ml with water, should be taken for analysis. The dilution water should be copper-free and contain 0.4 ml of HCl/200 ml of solution.

4 Normally, 2 ml of neocuproine solution is sufficient in a test. However, 4 ml of the reagent is suggested when the sample contains more than 100 µg of copper or when it is high in heavy metal ions.

**A-2.6.2** To the solution in the funnel add 25 ml of chloroform solvent (*see* Note) and shake the funnel vigorously for at least 1 min. Allow to stand for 5 min to permit the aqueous and chloroform layers to separate. Completely drain off the chloroform layer into a suitable, dry 50 ml Erlenmeyer Rask and add to it 10 ml of isopropyl alcohol to clear the solution.

NOTE — Isoamyl alcohol may be used in place of chloroform solvent for extraction purposes. Since the alcohol is lighter than water, the aqueous layer is discarded and the alcohol layer is collected in a suitable container to clear the solution. Add 10 ml of isopropyl alcohol Make spectrophotometric measurements at 454 nm when isoamyl alcohol is used.

**A-2.6.3** If the determination is to be made by means of Nessler tubes, transfer the organic extract to the Nessler tube. Dilute to the 50 ml mark with isopropyl alcohol, mix, and compare with previously prepared standards.

**A-2.6.4** If a photometer is to be used, measure the transmittance or absorbance of the organic test solution, using a mixture of 25 ml of chloroform solvent and 10 ml of isopropyl alcohol as the reference solution for the initial photometer setting. Make spectrophotometer measurements at a wave-length of 457 nm when chloroform is used. If the organic test solution is not sufficient to fill the optical cell, dilute the solution to 50 ml with isopropyl alcohol. The same dilution should be used, however, in **A-2.5**. Precision is decreased when the volume of the organic test solution is increased. The blank determination made for calibration purposes in **A-2.5** compensates for copper in both the reagents and the 200 ml of water. When the test sample contains less than 10 µg of copper it is important in **A-2.6.4** to compensate only for the copper in the reagents and not to include the few µg/litre of copper found in many supposedly copper-free waters. The reagent blank is found by extracting the copper from two 200 ml aliquots of copper-free water. Use the normal volumes of reagent in one and twice the normal volumes of hydrochloric acid, hydroxylamine and sodium acetate, and neocuproine solutions in the other. All reagents, including hydrochloric acid should be from the same bottles as those employed during the test on unknown samples. Measure the colour of the organic extract obtained from the blank treated with double the normal volumes of reagents, using the organic extract from the normal blank as reference solution for the initial photometer setting. Correct the value for copper in micrograms found in the unknown sample in **A-2.6.4** by subtracting from it the value for the reagent blank.

## **A-2.7 Calculation**

**A-2.7.1** Calculate the concentration of copper, in micrograms per litre as follows:

$$\text{Copper, } \mu\text{g/litre} = \frac{M \times 1000}{S}$$

where

M = mass of copper determined in accordance with **A-2.5** and **A-2.6** in µg, and

S = volume of sample used, in ml.

### **A-2.8 Range**

This method is applicable to the determination of copper in waters such as steam condensate and deionized water. It is specifically applicable to concentrations of copper from 2 µg/l to 1 000 µg/l.

## **A-3. DETERMINATION OF SILICA (COLORIMETRIC-MOLYBDATEREACTIVE SILICA)**

### **A-3.1 Outline of the Method**

**A-3.1.1** This method covers the photometric determination of molybdateresponsive silica in water. Due to the complexity of silica chemistry, the form of silica measured is defined by the analytical method as molybdate-reactive silica. Those forms of silica which are molybdate-reactive include dissolved simple silicates, monomeric silica and silicic acid, and an undetermined fraction of polymeric silica.

**A-3.1.2** This method is based on the reaction of the soluble silica with molybdate ion to form a greenish-yellow complex by reduction with 1-amino-2-naphthol-1-sulfonic acid.

### **A-3.2 Interferences**

**A-3.2.1** Colour and turbidity will interfere if not removed by filtration or dilution.

**A-3.2.2** The only specific substance known to interfere in the colour reaction is phosphate. Phosphate interference is eliminated by the addition of oxalic acid.

**A-3.2.3** A high dissolved salts concentration, such as in seawater or brine samples, can affect colour development. This can be compensated for by preparing standards in a matrix similar to that of samples or by using a standard additions technique.

**A-3.2.4** Strong oxidizing and reducing agents that may be found in some industrial waste waters may interfere in the reduction step of the reaction. Such waste waters may also contain organic compounds that may interfere in the colour formation.

### **A-3.3 Apparatus**

#### **A-3.3.1 *Spectrophotometer or Filter Photometer***

To obtain maximum sensitivity and reproducibility, a spectrophotometer suitable for measurements at 815 nm is required. Measurements may be made at 640 nm with a spectrophotometer or 640 nm to 700 nm with a filter photometer if less sensitivity is preferred.

#### **A-3.3.2 *Sample Cells***

The cell size to be used depends on the range covered and the particular instrument used. Longer path length cells (40 mm to 50 mm) are recommended for concentrations below 0.1 mg/l.

#### **A-3.4 *Reagents***

Store all reagents to be used in this method in polyethylene or other suitable plastic bottles.

#### **A-3.4.1** *Amino-Naphthol-Sulphonic Acid-Solution*

Dissolve 0.5 g of 1-amino-2-naphthol-4-sulphonic acid in 50 ml of a solution containing 1 g of sodium sulphite ( $\text{Na}_2\text{SO}_3$ ). After dissolving, add the solution to 100 ml of a solution containing 30 g of sodium hydrogen sulphite ( $\text{NaHSO}_3$ ). Make up to 200 ml and store in a dark, plastic bottle. Shelf life of this reagent may be extended by refrigerating. Solution should be adjusted to room temperature,  $25\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ , before use. Discard when the colour darkens or a precipitate forms.

#### **A-3.4.2** *Ammonium Molybdate Solution, 75 g/l*

Dissolve 7.5 g of ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) in 100 ml of water.

NOTE — Batch to batch variations in ammonium molybdate have been found to affect results of low concentrations (below 0.1 mg/l). High blanks, non-linear calibration curves, and poor reproducibility have been observed with some batches of this compound. When working with low concentrations of silica, a batch of ammonium molybdate known to produce reasonable blanks, linearity, and reproducibility should be set aside for this purpose.

#### **A-3.4.3** *Hydrochloric Acid (1 + 1)*

Mix 1 volume of concentrated hydrochloric acid (HCl, specific gravity 1.19) with 1 volume of water.

#### **A-3.4.4** *Oxalic Acid Solution (100 g/l)*

Dissolve 10 g of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) in 100 ml of water.

#### **A-3.4.5** *Silica Solution, Standard (1 ml = 0.1 mg $\text{SiO}_2$ )*

Dissolve 0.473 g of sodium metasilicate ( $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ ) in water and dilute to 1 litre.

### **A-3.5 Calibration and Standardization**

**A-3.5.1** Prepare a series of at least four standards covering the desired concentration ranges by proper dilution of the standard silica solution. Treat 50.0 ml aliquots of the standards in accordance with **A-3.6.1**. Prepare a blank using a 50.0 ml aliquot of water that has been similarly treated.

**A-3.5.2** For standards in the 20  $\mu\text{g/l}$  to 1 000  $\mu\text{g/l}$  range set the spectrophotometer at 815 nm and read the absorbance of each standard against the reagent blank. For standards in the 0.1 mg/l to 5 mg/l range, set the spectrophotometer at 815 nm (filter photometer 640 nm to 700 nm).

**A-3.5.3** Prepare a calibration curve for measurements at 815 nm by plotting absorbance versus concentration of silica in  $\mu\text{g/l}$  on linear graph paper. For measurements at 640 nm put absorbance versus silica concentration in mg/l.

### **A-3.6 Procedure**

**A-3.6.1** Transfer quantitatively 50.0 ml for an aliquot diluted to 50 ml of the sample that has been filtered through a 0.45  $\mu\text{m}$  membrane filter. If necessary, to remove turbidity to a polyethylene or



other suitable plastic container and add in quick succession 1 ml of hydrochloric acid ( 1 + 1 ) and 2 ml of the ammonium molybdate solution. Mix well. After exactly 5 min add 1.5 ml of oxalic acid solution and again mix well. After 1 min add 2 ml of amino-naphthol-sulphonic acid solution. Mix well and allow to stand for 10 min.

**A-3.6.2** Prepare a reagent blank by treating a 50.0 ml aliquot of water as given in **A-3.6.1**.

**A-3.6.3** Measure the absorbance of the sample at 815 nm against the reagent blank (or at 640 nm for higher concentrations).

### **A-3.7 Calculation**

**A-3.7.1** Silica concentration in micrograms  $\text{SiO}_3$ , per litre may be read directly from the calibration curve at 815 nm prepared in **A-3.5.3**. For measurements made at 640 nm, silica concentration may be read directly in milligrams  $\text{SiO}_2$  per litre from the calibration curve prepared in **A-3.5.3**.

**A-3.8 Range** - The useful range of this method is 20  $\mu\text{g/l}$  to 1000  $\mu\text{g/l}$  at higher wavelength (815 nm) and 0.1 mg/l to 5 mg/l at lower wavelength (640 nm). It is particularly applicable to treated industrial waters. It may be applied to natural waters and wastewaters following filtration or dilution, or both.

## **A-4 DETERMINATION OF SODIUM**

### **A-4.1 Outline of Method**

When a solution containing dissolved sodium is aspirated into a flame, a characteristic yellow-orange colour results. The intensity of this flame is a function of concentration. The flame filter photometer is the apparatus used for measuring the intensity of this emitted light.

### **A-4.2 Apparatus**

**A-4.2.1** *Filter Flame Photometer with Compressor*

**A-4.2.2** *Liquefied Petroleum Gas Cylinder with Regulator*

**A-4.2.3** *Gas Ignitor*

**A-4.2.4** *Polyethylene Tubes, for Gas and Air*

**A-4.2.5** *Filter for Sodium*

**A-4.2.6** *Beakers, 5 ml capacity.*

**A-4.2.7** *Spot Galvanometer*

### **A-4.3 Reagents**

#### **A-4.3.1** *Standard Sodium Solution*

Dissolve 2.542 g of sodium chloride in one litre of sodium-free water in a volumetric flask. This solution contains 1.000 mg of sodium in one millilitre. This can be diluted for the required standard solution and stored in polyethylene bottles as glass bottle will contaminate the solution.

### **A-4.4 Procedure**

#### **A-4.4.1** *Boiler Water*

**A-4.4.1.1** Standardization of filter flame photometer - Air supply for the burner is to be provided from the air compressor which should deliver dry, oil-free air at a pressure of about 0.1 MN/m<sup>2</sup>.

**A-4.4.1.2** Connect the instrument to power supply.

**A-4.4.1.3** Connect the compressor and the gas ignitor to the sockets in the cabinet.

**A-4.4.1.4** Turn the sensitivity control fully anti-clockwise.

**A-4.4.1.5** Insert the sodium filter.

**A-4.4.1.6** Switch on mains and wait for five minutes so that the amplifier is stabilised.

**A-4.4.1.7** Bring the pointer of the meter to zero by adjusting 'set zero'.

**A-4.4.1.8** Open the air control and adjust the pressure of air to 0.07 MN/m<sup>2</sup>.

**A-4.4.1.9** Turn the gas control and light the burner with the ignitor.

**A-4.4.1.10** Slowly turn the gas control till the blue flame is obtained. At the start the flame may be noisy. Wait for five minutes.

**A-4.4.1.11** Feed sodium-free distilled water through the atomiser. This is done by dipping the PVC capillary tube into a beaker of distilled water.

**A-4.4.1.12** Adjust zero.

**A-4.4.1.13** Aspirate 2 mg/l standard sodium solution and adjust the needle of the meter to 100 with the sensitivity control.

**A-4.4.1.14** Repeat steps given in **A-4.4.1.11** to **A-4.4.1.13** to ascertain the repeatability. This should be checked from time to time in a series of tests.

**A-4.4.1.15** Introduce the boiler water into a 5 ml beaker and aspirate the same.

**A-4.4.1.16** From the meter reading calculate sodium concentration in mg/l.

**A-4.4.1.17** If the meter reading exceeds 100 mg/l, suitably dilute the boiler water with sodium-free water.

**A-4.4.2** *Saturated Steam, Superheated Steam, Condensate Feed Water*

**A-4.4.2.1** Repeat steps given in **A-4.4.1.2** to **A-4.4.1.12** (setting up of the instruments after connecting the spot galvanometer to the main instrument). Check that the spot galvanometer is in line.

**A-4.4.2.2** Aspirate 0.1 ppm standard sodium solution and adjust the spot to '100' with the sensitivity control.

**A-4.4.2.3** Repeat steps given in **A-4.4.1.11** to **A-4.4.1.13** to ascertain the repeatability. This should be checked from time to time in a series of tests.

**A-4.4.2.4** Introduce condensed saturated steam or superheated steam or condensate of feed water (as the case may be) into a 5 ml beaker and aspirate the same.

**A-4.4.2.5** From the position of the spot calculate sodium concentration in mg/l.

NOTE - The instrument should be located in an area away from direct sun light, and be free of draft, dust and tobacco fumes. When low level of sodium is being determined precautions should be enforced against contamination originating from perspiration, soap, cleanser, cleaning mixtures and inadequately rinsed apparatus.

## **A-5 DETERMINATION OF HYDRAZINE**

### **A-5.1 Outline of the Method**

In acid medium, hydrazine reacts with  $\rho$ -dimethylaminobenzaldehyde to produce a yellow colour which is matched against that obtained with a series of standard hydrazine solutions

### **A-5.2 Apparatus**

**A-5.2.1** *Nessler Tubes*, 50 ml capacity

### **A-5.3 Reagents**

**A-5.3.1** *Dilute Hydrochloric Acid*, approximately 0.5 N.

**A-5.3.2** *Standard Hydrazine Solution*

Dissolve 0.328 g of hydrazine di-hydrochloride in 50 ml of approximately 0.5 N hydrochloric acid and dilute with the same acid to 1 000 ml. Before use, dilute 10 ml of the solution to 1 000 ml with the same acid (1 ml = 0.001 mg of hydrazine ( $N_2H_4$ )).

**A-5.3.3**  *$\rho$ -Dimethylaminobenzaldehyde Solution*

Dissolve 4.0 g of  $\rho$ -dimethylaminobenzaldehyde (special grade for hydrazine determination) in a mixture of 200 ml of methanol and 20 ml of concentrated hydrochloric acid.

### **A-5.4 Procedure**

**A-5.4.1.1** Hydrazine tends to be destroyed in neutral or alkaline solutions in contact with air. Hence it is essential that the sampling is done properly as given below and that the test is carried out immediately thereafter:

**A-5.4.1.2** Insert the outlet tube from an efficient stainless steel cooler to the bottom of a 250 ml bottle. Allow the water to flow until a representative sample is obtained, at a temperature ranging from 17 °C to 30 °C. Withdraw the outlet tube slowly and immediately stopper the bottle, avoiding trapping any air-bubbles.

**A-5.4.2** Into 9 Nessler tubes, each containing 15 ml of dilute hydrochloric acid, add 0 ml, 0.5 ml, 1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml, 6.0 ml, 8.0 ml and 10.0 ml of standard hydrazine solution. Make the volumes to 40 ml by adding distilled water and mix. In the 10<sup>th</sup> Nessler tube containing 15 ml of

dilute hydrochloric acid, pipette out a suitable volume of the sample (2 ml, 10 ml or 25 ml) and dilute to 40 ml with distilled water and mix.

**A-5.4.3** Now add to each of the Nessler tubes 10 ml of p-dimethylaminobenzaldehyde solution. Mix and after 10 min compare the colour of the sample with those of the standards.

#### **A-5.6 Calculation**

$$\text{Concentration of hydrazine (as N}_2\text{H}_4\text{), mg/l} = \frac{V_1}{V_2}$$

where

$V_1$  = volume of standard hydrazine solution required for matching the colour with the sample, in ml; and

$V_2$  = volume of the sample taken for the test, in ml.

#### **A-5.7 Range of Accuracy**

The method is suitable in the range 0 mg/l to 5 mg/l of hydrazine.