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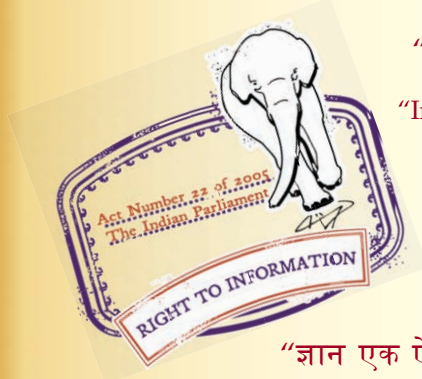
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IS 10496 (1983): Feed Water, Boiler Water and Condensate for High Pressure Boilers [CHD 13: Water Quality for Industrial Purposes]



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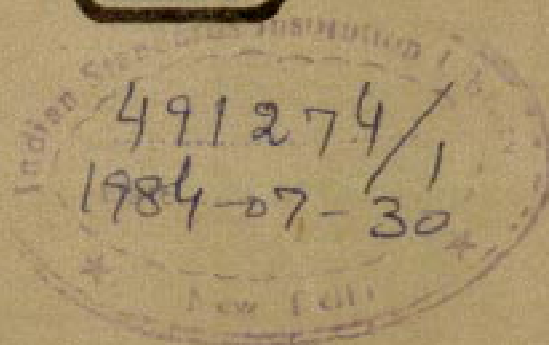
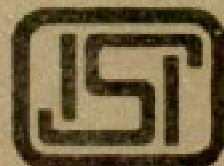


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Indian Standard
SPECIFICATION FOR FEED WATER,
BOILER WATER AND CONDENSATE
FOR HIGH PRESSURE BOILERS

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INDIAN STANDARDS INSTITUTION
MANAK BHAVAN, 9 BHADUR SHAH ZAFAR MARG
NEW DELHI 110002

Indian Standard

SPECIFICATION FOR FEED WATER, BOILER WATER AND CONDENSATE FOR HIGH PRESSURE BOILERS

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Indian Standard

SPECIFICATION FOR FEED WATER, BOILER WATER AND CONDENSATE FOR HIGH PRESSURE BOILERS

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 7 January 1983, after the draft finalized by the Boiler Water Sectional Committee had been approved by the Chemical Division Council.

0.2 The chief object of treatment of water for boilers is to prevent corrosion of the boiler and fittings and to prevent formation of scale. The chemical methods of attaining the desirable conditions in the water side of boilers operating above 5.9 MN/m^2 (60 kgf/cm^2) are given in IS : 4343-1983*. The earlier version of that standard, which was published in 1967, also prescribed the recommended chemical composition of feed water, boiler water and condensate for boilers operating above 4.1 MN/m^2 (42 kgf/cm^2). The Committee, however, while revising that standard decided to modify the specification of feed water, boiler water and condensate in light of the latest technological developments and publish the same as a separate standard.

0.3 In the preparation of this standard, considerable assistance has been drawn from BS 2486 : 1978 'Recommendations for treatment of water for land boilers', issued by the British Standards Institution.

0.4 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 : 2-1960†. 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

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

1.1.1 The requirements prescribed are for boilers operating at pressures above 5.9 MN/m^2 (60 kg/cm^2) during normal operation of the unit with

*Code of practice for treatment of water for high pressure boilers (*first revision*).

†Rules for rounding off numerical values (*revised*).

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. REQUIREMENTS

2.1 Water-Tube Boilers (Drum Type) — The feed water, boiler water and condensate, for water-tube boilers shall comply with the requirements given in Table 1.

NOTE — In case of recovery boilers operating at low boiler pressures of 1.5 to 2.0 MN/m² 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/m² 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.

2.1.1 Recommendation for Application of Requirements Given in Table 1 — While applying the requirements given in Table 1 the following additional factors should also be kept in view:

- a) *pH value of feed water* — With cuprous feed heaters the range of pH values should be limited to 8.5 to 9.2 and without cuprous feed heaters to 9.2 to 9.5. For spray attemperation, the feed water should be dosed only with volatile chemical, if necessary; caustic soda should be injected direct to the boiler drum.
- b) *Oxygen* — The oxygen limits in Table 1 are those obtained after physical deaeration. In addition to physical deaeration, the use of a chemical oxygen scavenger is recommended.

Sodium sulphite should not be used in boilers operating above 5.9 MN/m² (60 kg/cm²) except where hydrazine cannot be used and then only if strict control is maintained to prevent damage due to its breaking down.

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

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 per cent complete before entry to the boiler. Thus, for smaller industrial plants, sodium sulphite would generally be preferred.

In boiling water, concentration of hydrazine is very low above 7.8 MN/m² (80 kg/cm²) because, owing to its decomposition and/or volatilization, the low concentrations remaining in the boiler water are extremely difficult to determine and thus boiler water concentration is not a practical basis for controlling the

TABLE 1 REQUIREMENTS FOR FEED WATER, BOILER WATER AND CONDENSATE FOR WATER-TUBE BOILERS (DRUM TYPE)

(Clauses 2.1 and 2.1.1)

Sl. No.	CHARACTERISTIC	REQUIREMENTS FOR BOILER PRESSURE MN/m ² (in the drum)				METHODS OF TEST, REF TO CL No. OF		SEE ALSO CL No.
		6·0-7·8	7·9-9·8	9·9-11·8	above 11·8	IS : 3550-1965*	IS : 3025-1964†	
(1)	()	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	Feed Water at Economizer Inlet							
→ i)	Total hardness (as CaCO ₃), mg/l, <i>Max</i>	Nil	Nil	Nil	Nil	—	16.1	—
ii)	pH value (<i>see also</i> Note 1)	8·5-9·5	8·5-9·5	8·5-9·5	8·5-9·5	—	8	2.1.1 (a)
iii)	Oxygen, (as O ₂), mg/l, <i>Max</i>	0·01	0·005	0·005	0·005	25	—	2.1.1 (b)
iv)	Iron+copper mg/l, <i>Max</i>	0·02	0·01	0·01	0·01	(<i>see A-1 and A-2</i> for methods of test)		2.1.1 (c)
v)	Silica (SiO ₂), mg/l, <i>Max</i>	0·05	0·02	0·02	0·02	(<i>see A-3</i> for method of test)		2.1.1 (d)
vi)	Oil. mg/l, <i>Max</i>	Nil	Nil	Nil	Nil	—	59	—
vii)	Residual hydrazine (as N ₂ H ₄), mg/l, <i>Max</i>	0·05	0·05	0·05	0·05	26	—	—
viii)	Conductivity, after passing through cation exchange column at 25°C, microsiemens/ cm, <i>Max</i>	0·5	0·3	0·3	0·3	7	—	—
→ ix)	Oxygen consumed in 4 hours, mg/l, <i>Max</i> (<i>see also</i> Note 2)	Nil	Nil	Nil	Nil	—	51	—

*Methods of test for routine control for water used in industry.

†Methods of sampling and test (physical and chemical) for water used in industry.

(Continued)

TABLE 1 REQUIREMENTS FOR FEED WATER, BOILER WATER AND CONDENSATE FOR WATER-TUBE BOILERS (DRUM TYPE) — Contd

Sl No.	CHARACTERISTIC	REQUIREMENTS FOR BOILER PRESSURE MN/m ² (in the drum)				METHODS OF TEST, REF TO CL NO. OF		SEE ALSO CL No.
		6·0-7·8	7·9-9·8	9·9-11·8	above 11·8	IS: 3550- 1965*	IS: 3025- 1964†	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Boiler Water								
i)	Phosphate (as PO ₄), mg/l (see also Note 3)	5-20	5-20	5·10	2·10	14	—	—
ii)	Caustic alkalinity (CaCO ₃), mg/l, Max (see also Note 3)	20	7	5	2	—	15	2.1.1 (a)
iii)	Total alkalinity (as CaCO ₃), mg/l, Max	50	30	20	15	—	13	2.1.1 (e)
iv)	Silica (as SiO ₂), mg/l, Max (see also Note 4)	10	5	2	1	(see A-3 for method of test)	—	2.1.1 (f)
v)	Total hardness (as CaCO ₃) mg/l, Max	Nil	Nil	Nil	Nil	—	16.1	—
vi)	Hydrazine (as N ₂ H ₄), mg/l	0·05-0·1	<0·01	<0·005	<0·005	26	—	2.1.1 (b)
vii)	Total dissolved solids, mg/l, Max	120	100	75	50	(see A-4 for method of test)	—	2.1.1 (c)
viii)	Chloride, mg/l, (as NaCl), Max	6	4	2	2	(see A-5 for method of test)	—	—
ix)	pH value (see also Note 3)	10-11	10-11	9·5-10·5	9·5-10·5	—	8	—

Condensate

i) pH value	8.5-9.0	8.5-9.0	8.5-9.0	8.5-9.0	—	8	—
ii) Hardness (as CaCO_3), n <i>Max</i>	Nil	Nil	Nil	Nil	—	16.1	—
iii) Oil, mg/l, <i>Max</i>	Nil	Nil	Nil	Nil	—	59	—
iv) Silica (as SiO_2), mg/l, <i>Max</i>	0.02	0.02	0.02	0.02	(see A-3 for method of test)		—
v) Iron + copper, mg/l, <i>Max</i>	0.01	0.005	0.005	0.005	(see A-1 and A-2 for methods of test)		—
vi) Ammonia (as NH_3), mg/l, <i>Max</i>	0.5	0.5	0.5	0.5	23	—	—
vii) Sodium (as Na), mg/l, <i>Max</i>	0.06	0.03	0.02	0.02	(see A-6 for method of test)		—
viii) Dissolved oxygen (as O_2), mg/l, <i>Max</i> (see also Note 5)	0.03	0.03	0.03	0.03	25	—	—

NOTE 1 — When feed water heaters are of copper or copper alloy construction, the pH of the feed water should be maintained between 8.5 and 9.2 while when feed water heaters are of iron construction, the pH of the feed may be maintained between 8.5 and 9.5.

NOTE 2 — This test should be conducted after neutralization of the hydrazine or sulphite, when present, which will also absorb permanganate. A blank with distilled water (see IS: 1070-1977†) should be carried out along with the sample.

NOTE 3 — To be chosen by the user in agreement with the boiler manufacturer. pH also will be as per the manufacturer's specification.

NOTE 4 — For thermal power boilers the silica content of water has to be maintained such that the silica content of steam conforms to the requirements as given in Fig. 1 and Fig. 2 or as per the manufacturer's specifications.

NOTE 5 — As determined at turbine condensate extraction pump. Not to be determined for process condensate.

*Methods of test for routine control for water used in industry.

†Methods of sampling and test (physical and chemical) for water used in industry.

‡Specification for water for general laboratory use (second revision).

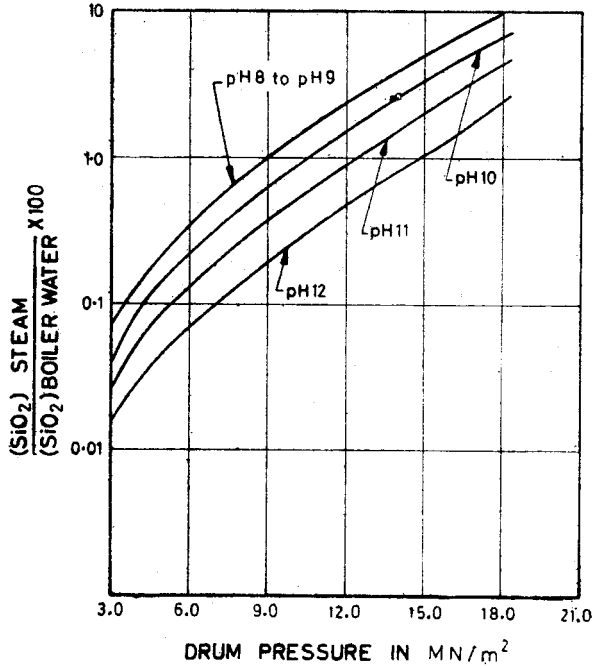


FIG. 1 PERCENTAGE OF SILICA IN STEAM
VERSUS BOILER DRUM PRESSURE
AT SELECTED BOILER WATER pH

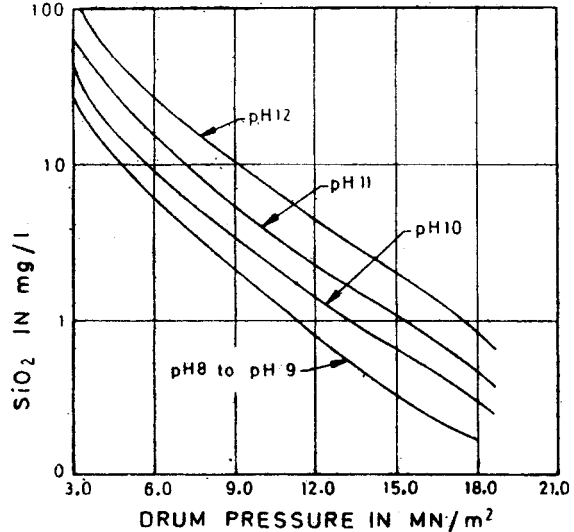


FIG. 2 MAXIMUM BOILER WATER SILICA
CONCENTRATION VERSUS DRUM PRESSURE
AT SELECTED BOILER WATER pH

dose; in such cases, hydrazine should be dosed in 100 percent excess over the residual oxygen after physical deaeration.

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. The use of sodium sulphite may also be unacceptable in some of these applications.

- c) *Iron and Copper* — The maxima for the sum of these impurities should be regarded as concentrations not to be exceeded, if possible, during continuous running conditions.
- d) *Solids, Alkalinity and Silica in Feed Water* — The concentrations of these impurities 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 solid matter and silica as possible. In general, the spray attemperator should not be fed with water containing more than 1 mg/l solid matter (in order to prevent deposition in the superheater). Where the superheater contains an austenitic steel section, the solids in the spray water should be less than 0.1 mg/l. When steaming a turbine, the spray water should contain less than 0.02 mg/l silica.

NOTE — A certain amount of alkali is added to maintain the desired alkalinity in the boiler feed water. The alkali to be used may be amines or ammonia. A volatile amine such as cyclohexylamine or morpholine may also be added (for methods of test, see A-7 and A-8). Amines make the condensate alkaline.

- e) *Solids and Alkalinity in Boiler Water* — The maxima for total alkalinity, suspended solids and dissolved solids are set in relation to steam purity. Exceeding these values may lead to carryover of boiler water with the steam. Owing to the risk of on-load corrosion at pressures in excess of about 7.8 MN/m² (80 kg/cm²), it is recommended that operation be at the lowest practicable concentrations of impurities.
- f) *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/m² (80 kg/cm²).

2.2 Once-Through Boilers — The feed water for once-through boilers shall comply with the requirements given in Table 2.

2.2.1 In general, once-through boilers require a feed water containing a minimum concentration of solid matter in order to prevent scaling and deposition. The conditions given in Table 2 are generally acceptable for normal continuous operation. Higher values may often be tolerated for short periods such as during start-up. The acceptable deviation from the

values given depends on the plant design, for example, the diameter of boiler tubes, the provision for blowing down and the extent and nature of condensate polishing.

2.2.2 The values given in Table 2 generally permit operation for at least three years before acid cleaning. Guidance on whether cleaning is necessary should be obtained from regular analysis for solid matter entering with the feed water. However, the continuous conversion of the tube surface to magnetite may be equally important in determining the frequency of acid cleaning as magnetite (magnetic iron oxide (Fe_3O_4)) is less dense than steel and the tube bore is directly reduced. This build up may cause a significant increase in pressure drop over the unit, thus requiring a higher feed water inlet pressure for the same outlet condition.

TABLE 2 REQUIREMENTS FOR FEED WATER FOR ONCE-THROUGH BOILERS (AT ECONOMIZER INLET)

(Clauses 2.2, 2.2.1 and 2.2.2)

Sl No.	CHARACTERISTIC	REQUIREMENT	METHOD OF TEST, REF TO CL No. OF	
			IS : 3550-1965*	IS : 3025-1964†
(1)	(2)	(3)	(4)	(5)
i)	Total solids, mg/l, <i>Max</i>	0.05	—	10
ii)	Oxygen after physical deaeration (as O_2), mg/l, <i>Max</i>	0.005	25	—
iii)	Silica (as SiO_2), mg/l, <i>Max</i>	0.02	(see A-3 for method of test)	
iv)	Iron (as Fe), mg/l, <i>Max</i>	0.01	(see A-1 for method of test)	
v)	Caustic alkalinity, mg/l	Nil	—	15
vi)	Copper plus nickel (as Cu+Ni), mg/l, <i>Max</i>	0.002	(see A-2 and A-9 for methods of test)	
vii)	Hardness (as CaCO_3), mg/l, <i>Max</i>	Nil	—	16.1
viii)	Suspended solids, mg/l, <i>Max</i>	Nil	—	12
ix)	pH value with cuprous feed heaters	8.5-9.2	—	8
x)	pH value without cuprous feed heaters	9.2-9.5	—	8

*Methods of test for routine control for water used in industry.

†Methods of sampling and test (physical and chemical) for water used in industry.

2.2.3 In consequence, the concentrations of solid matter in the feed water should be kept within strictly regulated limits and the dosing of volatile chemicals for adjustment of the pH value should also be precise, with no excessive over-dosing.

2.2.4 The feed water should be continuously dosed with hydrazine in 100 percent excess over the oxygen concentration (measured after physical

deaeration) and with ammonia or a neutralizing amine to raise the pH value of the feed water to the specified range (pH range as is found by trial and analysis) to minimize the concentration of iron, copper and nickel in the condensate.

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.

3. SAMPLING

3.1 Representative samples of feed water, boiler water and condensate shall be obtained as directed in 2 of IS : 3025-1964*. In particular, the following directions shall be observed.

3.1.1 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.

3.1.2 Samples of feed water shall be obtained from the discharge of feed pump; samples of boiler 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 3.1.1 and collected in plastic or polyvinyl chloride bottles and stoppered immediately.

APPENDIX A

(Clause 2.1.1 and Tables 1 and 2)

METHODS OF TEST

A-1. DETERMINATION OF IRON (PHOTOMETRIC BATHOPHEN-ANTHROLINE 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

*Methods of sampling and test (physical and chemical) for water used in industry.

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/litre (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 five times with iron-free water. Before use, and after use (before again using), clean all glassware by making an iron extraction in each piece (without separating the alcoholwater 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 0.0835 g of 4.7-diphenyl 1, 10-phenanthroline in 100 ml of ethyl alcohol (95 percent).

A-1.4.5 Hydrochloric Acid (1 + 1) — Cautiously add 500 ml of HCl (sp gr 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/litre) — 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 dropwise 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 μg 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 to 80 $\mu\text{g}/\text{litre}$ 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) dropwise 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 minute, 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) dropwise with mixing until a distinct turbidity forms. Add hydrochloric acid (1 + 9) dropwise 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:

$$\text{Iron, } \mu\text{g/litre} = (M \times 1\,000\,000) / S$$

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 $\mu\text{g/l}$ 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 454 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 (CHCl_3) with 1 volume of isopropyl alcohol.

A-2.4.2 Copper, Standard Solution (1 ml = 4 μg copper as Cu) — Dilute 200 ml of copper solution (1 ml = 0.02 mg Cu) to 1 litre with water. One millilitre of this standard solution contains 4 μg of copper or, when diluted to 200 ml with water, it contains 20 μg of copper.

A-2.4.3 Hydrochloric Acid (*sp gr* 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 ml = 4 μg 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 μg) 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 μg).

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 to 30°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 to 4 ml of neocuproine solution (see Note 4) and shake the funnel and contents for 1 minute.

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

NOTE 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 to 80°C for 1 h by immersing the bottle up to the neck in hot water. Avoid heating the sample in a beaker to minimize possible contamination.

NOTE 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.

NOTE 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 minute. Allow to stand for 5 minutes to permit the aqueous and chloroform layers to separate. Completely drain off the chloroform layer into a suitable, dry 50-ml Erlenmeyer flask 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. Add 10 ml of isopropyl alcohol to clear the solution. 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 $\mu\text{g/litre}$ 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:

$$\text{Copper, } \mu\text{g/litre} = \frac{M \times 1\,000}{S}$$

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 to 1 000 $\mu\text{g/l}$.

A-3. DETERMINATION OF SILICA (COLORIMETRIC-MOLYBDATE-REACTIVE SILICA)

A-3.1 Outline of the Method

A-3.1.1 This method covers the photometric determination of molybdate-reactive 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 which in turn is converted to a blue 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 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 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 (Na_2SO_3). After dissolving, add the solution to 100 ml of a solution containing 30 g of sodium hydrogen sulphite (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, $25 \pm 5^\circ\text{C}$, 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, sp gr 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 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 one 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 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 to 5 mg/l range, set the spectrophotometer at 815 nm (filter photometer 640 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 μm 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 minutes add 1.5 ml of oxalic acid solution and again mix well. After 1 minute add 2 ml of amino-naphthol-sulphonic acid solution. Mix well and allow to stand for 10 minutes.

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 SiO₂ 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 SiO₂ per litre from the calibration curve prepared in A-3.5.3.

A-3.8 Range — The useful range of this method is 20 to 1 000 µg/l at higher wavelength (815 nm) and 0.1 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. DISSOLVED SOLIDS

A-4.1 Electrical Conductivity Methods — For water containing a given mixture of mineral salts, the electrical conductance is closely proportional to the dissolved solids. When the samples are known to be free from wide fluctuation in mineral content, the electrical conductance offers a quick means of computing the total dissolved solids. However, this procedure may be used only after ascertaining the appropriate conversion factor $\left(\frac{\text{Electrical conductance}}{\text{Dissolved solids}} \right)$ for a particular series of samples.

A-4.2 Procedure — Examine a number of samples gravimetrically as prescribed in 10 of IS : 3025-1964* for total dissolved solids and determine their electrical conductance also as prescribed in 9 of IS : 3025-1964*. Plot the figures so obtained on a graph and calculate the factor of relationship between the two. This factor may be checked and verified after every three months.

A-5. DETERMINATION OF CHLORIDES (LOW RANGE) — COLORIMETRIC METHOD

A-5.1 Outline of the Method — Solutions of ferric ammonium sulphate and mercuric thiocyanate are added to the sample. The chloride ion reacts with the mercuric thiocyanate to produce thiocyanate ion which in turn combines with ferric to form red ferric thiocyanate. The intensity of the colour which is proportional to the concentration of the chloride ions, is measured photometrically at a wavelength of 463 nm, or by visual comparison with standard solutions.

A-5.2 Interferences — Bromides, iodides, cyanides, thiosulphates, hydrazine, and nitrites interfere in this method. Colour, if present in the sample, will interfere with visual comparison and depending upon its spectral absorbance may interfere with the photometric measurement.

*Methods of sampling and test (physical and chemical) for water used in industry.

A-5.3 Apparatus

A-5.3.1 Nessler Tubes or Photometer — A set of 50-ml matched Nessler tubes or a photometer suitable for measurements at a wavelength of 463 nm, may be used for evaluating the intensity of the colour produced.

A-5.4 Reagents

A-5.4.1 Ferrous Ammonium Sulphate — Dissolve 5.0 g of ferrous ammonium sulphate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] in 20 ml of water. Add 38 ml of concentrated nitric acid (HNO_3 sp gr 1.42) and boil to oxidize the iron and remove the oxides of nitrogen. Dilute to 100 ml with halide-free water.

A-5.4.2 Mercuric Thiocyanate Methanol Solution (3 g/l) — Dissolve 0.30 g of mercuric thiocyanate [$\text{Hg}(\text{CNS})_2$] in 100 ml of methanol. Store in amber bottles. Allow to stand for at least 24 h before using. Do not use if more than 4 weeks old.

NOTE 1 — Caution — Mercuric salts are very poisonous. Due precautions should be observed when using this material.

NOTE 2 — A slight precipitate may form and settle out after 24 h. Care should be taken so that this precipitate is not resuspended when using the reagent. Only the clear, supernatant liquid should be used.

A-5.4.3 Sodium Chloride Solution Standard (10 mg Cl/l) — Dry several grams of sodium chloride (NaCl) for 1 h at 600°C. Prepare a stock solution by dissolving exactly 1.649 g of the dry salt in water and dilute to 1 litre. Prepare the standard solution as needed by diluting 10 ml of the stock solution to 1 litre with halide-free water. The resulting standard contains 10 mg of chloride ion per litre.

A-5.5 Calibration

A-5.5.1 Prepare a series of reference standards by diluting suitable volumes of the standard chloride solution with halide-free water. The temperature of the solutions used for calibration should be the same as that of the sample to be tested.

A-5.5.2 Treat each reference standard as described in A-5.6.

A-5.5.3 Prepare a calibration curve by plotting the readings on the photometer versus the concentration of chlorides. When the scale of the photometer reads directly in absorbance, plot the curve on rectilinear paper. When the scale reads in transmittance, it is convenient to plot the results on semilog paper, using the single cycle log axis to plot transmittance and the linear axis to plot the concentrations.

A-5.6 Procedure

A-5.6.1 Transfer 25 ml of sample to a glass stoppered cylinder and add successively 5 ml of ferric alum solution and 2.5 ml of mercuric thiocyanate solution. Mix thoroughly and allow to stand for 10 minutes.

A-5.6.2 Measure the intensity of the colour formed either by comparison with suitable reference standards in Nessler tubes or by a photometer. Adjust the zero setting of the photometer by using 25 ml of halide-free water tested in accordance with A-5.6.1.

NOTE — Since chloride ion is a very common contaminant, exercise extreme care in the collection and processing of the sample.

Soak all new glassware in hot nitric acid (1+19) for several hours. To be certain that new glassware is conditioned for the test run a chloride determination on halide-free water. After the run rinse the glassware thoroughly. Soak the glassware in halide-free water between tests. Discard all glassware that appears etched or scratched.

A-5.7 Calculation — Determine the amount of chloride ion in mg in the sample either by direct visual comparison with reference standards or by use of a suitable calibration curve.

A-5.8 Range — This method may be applied to waters containing chloride ion in concentrations from 0.10 to 10 mg/l. It is particularly useful for analysis of boiler water, boiler feed water, distillate, condensate and other relatively pure waters where low chloride concentrations are required to be determined accurately.

A-6. DETERMINATION OF SODIUM

A-6.1 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-6.2 Apparatus

A-6.2.1 *Filter Flame Photometer with Compressor*

A-6.2.2 *Liquefied Petroleum Gas Cylinder with Regulator*

A-6.2.3 *Gas Ignitor*

A-6.2.4 *Polyethylene Tubes for Gas and Air*

A-6.2.5 *Filter for Sodium*

A-6.2.6 *Beakers* — 5 ml capacity.

A-6.2.7 *Spot Galvanometer*

A-6.3 Reagents

A-6.3.1 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-6.4 Procedure

A-6.4.1 Boiler Water

A-6.4.1.0 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/m².

A-6.4.1.1 Connect the instrument to power supply.

A-6.4.1.2 Connect the compressor and the gas ignitor to the sockets in the cabinet.

A-6.4.1.3 Turn the sensitivity control fully anti-clockwise.

A-6.4.1.4 Insert the sodium filter.

A-6.4.1.5 Switch on mains and wait for five minutes so that the amplifier is stabilised.

A-6.4.1.6 Bring the pointer of the meter to zero by adjusting 'set zero'.

A-6.4.1.7 Open the air control and adjust the pressure of air to 0.07 MN/m².

A-6.4.1.8 Turn the gas control and light the burner with the ignitor.

A-6.4.1.9 Slowly turn the gas control till the blue flame is obtained. At the start the flame may be noisy. Wait for five minutes.

A-6.4.1.10 Feed sodium-free distilled water through the atomiser. This is done by dipping the PVC capillary tube into a beaker of distilled water.

A-6.4.1.11 Adjust zero.

A-6.4.1.12 Aspirate 2 mg/l standard sodium solution and adjust the needle of the meter to 100 with the sensitivity control.

A-6.4.1.13 Repeat steps given in A-6.4.1.10 to A-6.4.1.12 to ascertain the repeatability. This should be checked from time to time in a series of tests.

A-6.4.1.14 Introduce the boiler water into a 5-ml beaker and aspirate the same.

A-6.4.1.15 From the meter reading calculate sodium concentration in mg/l.

A-6.4.1.16 If the meter reading exceeds 100, suitably dilute the boiler water with sodium-free water.

A-6.4.2 Saturated Steam, Superheated Steam, Condensate Feed Water

A-6.4.2.1 Repeat steps given in **A-6.4.1.1** to **A-6.4.1.11** (setting up of the instruments after connecting the spot galvanometer to the main instrument). Check that the spot galvanometer is in line.

A-6.4.2.2 Aspirate 0.1 ppm standard sodium solution and adjust the spot to '100' with the sensitivity control.

A-6.4.2.3 Repeat steps given in **A-6.4.1.10** to **A-6.4.1.12** to ascertain the repeatability. This should be checked from time to time in a series of tests.

A-6.4.2.4 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-6.4.2.5 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-7. DETERMINATION OF MORPHOLINE

A-7.1 Outline of the Method — Carbon disulphate and morpholine react to form a thiocarbamate which reacts with an excess of copper to form an amber to brown complex. The intensity of the colour is proportional to the amount of morpholine in the water. In order to obtain the reaction with carbon disulphide the solution should have a pH of approximately 9.5 ± 0.1 at 25°C.

A-7.2 Interferences

A-7.2.1 Except for hydrazine substances normally present in boiler feed-water and steam do not interfere with this test. Hydrazine causes positive interference. Addition of formaldehyde to the sample aliquot eliminates this effect.

A-7.2.2 The basic reactions of the test are common to otadecylamine and other long chain aliphatic amines, as well as to short chain primary, secondary, and tertiary amines.

A-7.3 Apparatus

A-7.3.1 Filter Photometer or Spectrophotometer — Suitable for measurements at a wavelength of 430 nm.

A-7.3.2 Shaker — Reciprocating adjusted for shaking at the rate of about 280 oscillations per minute with a horizontal stroke of about 5 cm.

A-7.4 Reagents

A-7.4.1 Carbon Disulphate (CS_2)

A-7.4.2 Copper Sulphate Solution (2.0 g/l) — Dissolve 2.0 g of copper sulphate ($CuSO_4 \cdot 5H_2O$) in water and dilute to one litre.

A-7.4.3 Formaldehyde (HCHO, 37 percent)

A-7.4.4 Hydrochloric Acid, Standard (0.5 N) — Prepare and standardize.

A-7.4.5 Methyl Red Indicator Solution (1 g/l)

A-7.4.6 Sodium Borate Solution (40 g/l) — Prepare a solution, saturated at room temperature, of 40 g of sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) per litre. Adjust the pH of this solution to 9.5 at 25°C using 0.5 N sodium hydroxide solution.

A-7.4.7 Sodium Hydroxide Standard Solution (0.5 N) — Prepare and standardize.

A-7.4.8 Wetting Agent Solution

A-7.4.9 Morpholine Standard Solution (1 ml = 0.001 g morpholine) — Weigh 1.099 g of 91 percent morpholine using a weighing bottle, wash into a 1-litre volumetric flask and dilute to volume with water. If the morpholine is not 91 percent, apply the appropriate factor in preparing the standard solution. Check the strength of the undiluted morpholine as given in A-7.4.9.1.

A-7.4.9.1 Pipette 50 ml of 0.5 N hydrochloric acid into a 250-ml Erlenmeyer flask. Add 1 drop of methyl red indicator solution and from a tared Lunge pipette, add up to 2 g of the morpholine directly into acid. Reweigh the Lunge pipette to determine the sample size. Swirl the flask and observe the colour of the solution which should be pink or red; a yellow-coloured solution indicates that the sample size is excessive. Heat the solution to boiling and boil gently for approximately 1 minute to remove carbon dioxide. Titrate immediately with 0.5 N sodium hydroxide solution to the yellow end point. Calculate percent morpholine as follow:

$$\text{Morpholine, percent} = [(A \times a) - (B \times b) \times 8.712] / S$$

where

A = volume of hydrochloric acid used in ml;

a = normality of the hydrochloric acid;

B = volume of the sodium hydroxide solution required for titration of the sample, in ml;

b = normality of the sodium hydroxide solution; and

S = mass of sample used in g.

A-7.5 Preparation of Calibration Curve

A-7.5.1 Prepare a series of morpholine standards by diluting 1, 2, 3, 4 and 5 ml of the morpholine standard solution to one litre with water in 1-litre volumetric flasks. These standards contain 1, 2, 3, 4, and 5 mg/l respectively.

A-7.5.2 Treat 100 mg/l of each reference standard in accordance with A-7.6.

A-7.5.3 Prepare a calibration curve by plotting the readings on the photometer versus the concentration of morpholine. When the scale of the photometer reads directly in absorbance plot the results on rectilinear paper. When the scale reads in transmittance plot the results on semilog paper using the single cycle log axis to plot transmittance and the linear axis to plot the concentrations.

A-7.6 Procedure

A-7.6.1 Pipette 100 ml of sample into a 250-ml glass bottle having a polyethylene-lined cap. Add 1 drop of formaldehyde and shake vigorously for 15 s. Add successively 5 ml of saturated sodium borate solution and 2 drops of carbon disulphide. Mix thoroughly by shaking for 15 minutes on a shaker.

A-7.6.2 Add 1 ml of copper sulphate solution, shake vigorously by hand for 30 s, let stand for 1 minute and then add 1 drop of wetting agent solution from a dropper having a 3-mm opening.

A-7.6.3 Mix thoroughly by shaking for 4 minutes on the shaker, remove, and pour contents into a 125-ml separatory funnel. Allow to stand for 1 minute, shake vigorously by hand for 15 s, and let stand for 1 minute.

A-7.6.4 Draw off the sample and read the intensity of the colour in a filter photometer or spectrophotometer within 3 to 5 minutes. Adjust the photometer to zero absorbance or 100 percent transmittance by using 100 ml of sample and the procedure as described but omit adding of carbon disulphide.

A-7.6.5 Determine the morpholine content of the sample directly from the calibration curve prepared in accordance with A-7.5.

A-7.7 Calculation

A-7.7.1 Calculate the concentration of morpholine in milligrams per litre as follows:

$$\text{Morpholine, mg/l} = M \times 100/S$$

where

M = milligrams per litre of morpholine read from calibration curve, and

S = millilitres of sample used.

A-7.8 Range — The method may be used to monitor the concentration of morpholine in steam and condensate. The method is applicable to waters containing morpholine in concentrations from 1 to 5 mg/l. Higher concentrations may be determined by dilution.

A-8. DETERMINATION OF CYCLOHEXYLAMINE

A-8.1 Outline of the Method — The method is based on the diazotization of *p*-nitroaniline with sodium nitrite in the presence of hydrochloric acid and the subsequent coupling of the diazonium chloride formed with cyclohexylamine to produce a strongly coloured, reddish compound. The red compound is extracted with isoamyl alcohol for concentration and reduction of background colour. The colour of the extract is measured photometrically after treatment with an alcoholic solution of sodium hydroxide.

A-8.2 Interferences — None of the constituents present in the usual feed-water causes difficulty in the method. As much as 1 to 2 mg/l of iron can be tolerated. Morpholine does not interfere. Ammonia produces a reaction similar to cyclohexylamine, however, at 530 nm at which the colour is measured 6 to 7 mg/l of ammonia is required to produce the same absorbance as 1 mg/l of cyclohexylamine. Less ammonia can be tolerated if the colour is measured at a wavelength lower than 530 nm. One mg/l of hydrazine produces a positive error in the test equivalent to 0.5 mg/l of cyclohexylamine. Neither triethanolamine nor triethylamine interfere, but monoethanolamine is measured in the test.

A-8.3 Apparatus

A-8.3.1 Filter photometer or spectrophotometer suitable for measurements at a wavelength of 530 nm.

A-8.4 Reagents

A-8.4.1 Buffer Solution — Dissolve 50 g of potassium hydroxide (KOH) and 70 g of boric acid (H_3BO_3) in about 700 ml of water. Dilute solution to one litre with water.

A-8.4.2 Cyclohexylamine, Standard Solution (1 ml = 0.1 mg cyclohexylamine) — Prepare a stock solution by weighing 1.00 g of technical cyclohexylamine (purity over 99 percent) in a weighing bottle, transferring the material to about 800 ml of water and diluting the solution to one litre. Prepare the standard solution by diluting 100 ml of the stock solution to one litre with water.

A-8.4.3 Isoamyl Alcohol

A-8.4.4 Methyl Alcohol

A-8.4.5 Nitroaniline Solution (10 g/l) — Dissolve 1 g of p-nitroaniline in a mixture of 25 ml of hydrochloric acid (sp gr 1.19) and 75 ml of water.

A-8.4.6 Sodium Hydroxide Solution (80 g/l) — Dissolve 20 g of sodium hydroxide (NaOH) in 200 ml of water. Cool and dilute solution to 250 ml with water.

A-8.4.7 Sodium Hydroxide Alcoholic Solution (20 g/l) — Dissolve 20 g of sodium hydroxide (NaOH) in 150 ml of water. Add the solution to 800 ml of methyl alcohol and dilute in one litre with water.

A-8.4.8 Sodium Nitrite Solution (5.75 g/l) — Dissolve 0.565 g of sodium nitrite (NaNO_2) in water and dilute solution to 100 ml with water. Prepare solution fresh at least once every two weeks.

A-8.5 Photometer Calibration

A-8.5.1 Prepare a series of cyclohexylamine standards to contain 1 to 10 mg/l by diluting 0.10 ml of standard cyclohexylamine solution to 100 ml with water.

A-8.5.2 Develop colour in the series of standards as directed in **A-8.6**. Measure the absorbance of the alcoholic extract obtained from each standard in a 25 mm or 20 mm cell at 530 nm with a photometer. For the initial photometer setting to zero use methyl alcohol as the reference solution.

A-8.5.3 Plot absorbance versus concentration of cyclohexylamine in mg/l on linear graph paper. A line that deviates only slightly from being straight should be obtained.

A-8.6 Procedure

A-8.6.1 Pipette into a clean 250-ml separatory funnel, 1 ml of nitroaniline solution and 1 ml of sodium nitrite solution. Immediately cap and swirl the funnel to mix contents. Between 2 and 3 minutes after the mixing step add 100 ml of the sample, if necessary, cooled to room temperature. Cap the funnel, and shake to mix contents.

NOTE 1 — *Caution* — Use a safety pipette or burette to measure the nitroaniline solution.

NOTE 2 — Slightly lower cyclohexylamine values are obtained if a time interval longer than 3 minutes is allowed for the diazotization step.

A-8.6.2 Immediately add 10 ml of buffer solution, cap the funnel and shake several times to mix contents. The solution should have a pH of 9.0 ± 0.2 after addition of the buffer solution. Low results will be obtained at pH values below this level. Start a stop watch as soon as possible after mixing. At the end of 30 s add 4 ml of sodium hydroxide solution by means of a 10-ml graduated cylinder and mix the contents immediately.

NOTE — Time allowed for coupling is critical and stop watch accuracy in timing is needed. As much as 25 percent more colour is formed if 60 s are allowed for coupling. Colour fades appreciably after 60 s.

A-8.6.3 Add 10 ml of isoamyl alcohol by means of a graduated cylinder to the funnel. Invert funnel at least 20 times to extract the reddish-coloured compound into the alcohol. Avoid vigorous shaking since an emulsion can result. Permit the funnel to stand for about 5 minutes to allow the two layers to separate.

A-8.6.4 Transfer the bottom aqueous layer into a clean, separatory funnel. Retain the alcoholic layer in the original funnel. Make a second extraction of the aqueous layer by repeating **A-8.6.3** with an additional 10 ml of isoamyl alcohol. Discard the aqueous layer and add the alcoholic layer from the second extraction to the original funnel containing the first extract. Mix the two extracts by swirling the funnel and allow any water droplets to settle.

A-8.6.5 Pipette 5 ml of the alcoholic extract into a dry, Erlenmeyer flask (Caution *see* Note 1 under **A-8.6.1**). Add 45 ml of alcoholic caustic solution to the flask with a graduated cylinder. Mix the contents by swirling the flask.

A-8.6.6 Measure the absorbance of the red-coloured solution with a photometer using methyl alcohol as the reference solution for the initial photometer setting.

A-8.7 Calculation — Calculate the concentration of cyclohexylamine in milligrams per litre as follows:

$$\text{Cyclohexylamine, mg/l} = M \times (100/S)$$

where

M = concentration of cyclohexylamine indicated by the calibration curve in mg/l, and

S = volume of sample used in ml.

A-8.8 Range — This method may be used to monitor concentration of cyclohexylamine in steam condensate and feedwater. The method may be applied to waters containing cyclohexylamine in concentrations from 0.25 to 10 mg/l. Higher concentrations may be determined by dilution of sample.

A-9. DETERMINATION OF NICKEL

A-9.0 Principle — After destruction of organic matter, nickel is extracted from ammoniacal solution as its dimethylglyoxime complex and determined colorimetrically. The method is applicable for determining nickel content up to 100 μg .

A-9.1 Apparatus

A-9.1.1 Spectrophotometer — For use at wavelength 4 800 \AA or absorptiometer with a suitable blue filter or Nessler tubes, matched.

A-9.2 Reagents

A-9.2.1 Concentrated Ammonium Hydroxide — 20 percent m/m .

A-9.2.2 Sodium Citrate Solution — 25 percent (m/v).

A-9.2.3 Dimethylglyoxime Solution — Prepare a 1-percent (m/v) solution in dilute ammonia hydroxide (1 : 19 v/v).

A-9.2.4 Chloroform — Shake 500 ml of chloroform with 50 ml of hydrochloric acid (10 percent m/m). Allow the layers to separate, run the chloroform into another separating funnel and wash by shaking with water until free of acid.

A-9.2.5 Dilute Hydrochloric Acid — 1 : 19 (v/v).

A-9.2.6 Bromine Water — saturated.

A-9.2.7 Standard Nickel Solution — Dissolve 0.0479 g of nickel sulphate ($\text{NiSO}_4 \cdot 7\text{HO}$) in water containing 1 ml of sulphuric (1 N) and dilute with water to one litre. Prepare fresh each time. One millilitre of the solution contains 0.01 mg of nickel (as Ni).

A-9.3 Procedure

A-9.3.1 Take an aliquot of the digested sample and dilute to 100 ml. Add 10 ml of sodium citrate solution. Place a small piece of litmus paper in the solution and add concentrated ammonium hydroxide, with mixing, until it is just ammoniacal; add 10 drops in excess and transfer to a 250-ml separating funnel. Add 10 ml of dimethylglyoxime solution, shake for one minute and allow to stand for 10 minutes. Add 10 ml of chloroform, shake for one minute and allow the layers to separate. Remove the chloroform layer into another separating funnel, rising the stem of the funnel with about 3 ml of chloroform and adding it to the chloroform extract. Repeat the extraction of the aqueous layer with a further 10 ml of chloroform and add this to the previous extract, rinsing the stem as before. To the combined chloroform extracts, add 15 ml of dilute hydrochloric acid and shake vigorously for one minute. Allow the layers to separate. Draw the chloroform layer into another separating funnel and

repeat washing with another 5 ml of dilute hydrochloric acid. Reject the chloroform layer. Combine the two acid extracts and transfer to a 100-ml beaker rinsing the funnels with a few millilitres of water and adding it to the acid extract. Heat carefully over a low flame to expel any chloroform and boil to reduce the volume to about 25 ml. Cool and transfer to a 50-ml Nessler tube or calibrated flask rinsing the beaker twice, using 5 ml of water each time. Add in the order given 2 ml of sodium citrate solution, 2 ml of bromine water, just enough concentrated ammonium hydroxide to destroy the bromine colour and to give 1 ml excess, and 4 ml of dimethylglyoxime solution. Dilute to the 50 ml mark with water and mix.

A-9.3.2 Carry out a blank on the reagents used adopting the same procedure as for sample.

A-9.3.3 Measure the optical densities of the test and blank solutions in a spectrophotometer using a 4-cm cell and a wavelength of 4800 \AA or an absorptiometer with a suitable blue filter. Use water in the comparison cell. Read the nickel content equivalent to the observed optical densities of the sample and blank from a previously prepared calibration curve. Subtract the blank and obtain the nickel content of the sample. When a photometer is not available, the colours may be matched visually against standards in Nessler tubes.

A-9.3.4 Preparation of Calibration Curve — Pipette out appropriate volumes of standard nickel solution to cover the range 0 to $100 \mu\text{g}$ of nickel into a series of 50 ml Nessler tubes or volumetric flasks. Add to each 20 ml of dilute hydrochloric acid, 2 ml of sodium citrate solution, 2 ml of bromine water, just enough concentrated ammonium hydroxide to destroy the bromine colour and to give 1 ml excess, and 4 ml of dimethylglyoxime solution. Dilute each to the 50 ml mark, mix, measure the optical densities and construct the calibration curve by plotting absorbance values against nickel content in micrograms.

A-9.4 Calculation

$$\text{Nickel (as Ni), mg/l} = \frac{1000 \times 100 \times M}{V_1 \times V_2}$$

where

M = mass in mg of nickel which matches the colour obtained with the sample,

V_1 = volume in ml of the sample taken for the test, and

V_2 = volume in ml of the aliquot taken for the test.

INDIAN STANDARDS

ON

BOILER WATER

IS:

- 1680-1982 Code of practice for treatment of water for low and medium pressure land boilers (*third revision*)
- 1813-1961 Code of practice for treatment of water for marine boilers
- 2859-1977 Code of practice for treatment of water for locomotive boilers (*first revision*)
- 4343-1983 Code of practice for treatment of water for high pressure boilers (*first revision*)
- 7932-1982 Boilers water treatment compounds (*first revision*)
- 10496-1983 Feed water, boiler water and condensate for high pressure boilers

AMENDMENT NO. 1 SEPTEMBER 1994
TO
IS 10496 : 1983 SPECIFICATION FOR FEED WATER,
BOILER WATER AND CONDENSATE FOR HIGH
PRESSURE BOILERS

(*Page 25, clause A-7.4.1*) — Substitute the following for the existing clause:

'A-7.4.1 *Carbon Disulphide (CS₂)*'

(CHD 013)

20 SEP 1994

Reprography Unit, BIS, New Delhi, India