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Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER USED IN INDUSTRY

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MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
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Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER USED IN INDUSTRY

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 12 November 1964, after the draft finalized by the Water Sectional Committee had been approved by the Chemical Division Council.

0.2 Three Indian standards had been published regarding the methods of sampling and test (physical and chemical) for industrial water, namely, IS : 1620-1961*, IS : 1621-1963† and IS : 1631-1960‡. The Committee responsible for the preparation of these standards considered it desirable to amalgamate them into a single document; that has been done in the form of this standard. While amalgamating these standards, the text and the sequence of the clauses have been suitably realigned so as to make them rational and convenient for reference and use by the analyst. Further, wherever necessary, outline of the methods of test have also been introduced.

0.3 This standard has been prepared to guide water testing laboratories in testing industrial water. Though some of the methods prescribed may be applicable to sea water, and also sewage and industrial effluents, these have not been specifically covered.

0.4 Normal variations in processes and in equipment from plant to plant preclude the possibility of specifying standard methods of sampling that are applicable in all cases. Definite principles have, however, been established as a basis for the formulation of procedures for sampling which are applicable in general and probably applicable in most specific cases. Where modifications of these procedures are necessary, they may be made by the exercise of trained judgement in each individual case.

0.5 In the preparation of this standard, considerable assistance has been derived from the following publications:

International standards for drinking-water. World Health Organisation, 1958. Geneva.

*Methods of test (chemical) for industrial water.

†Methods of sampling of industrial water for physical and chemical examination.

‡Methods of test (physical) for industrial water.

B.S. 1427 : 1949 Tests for water used in steam generation. British Standards Institution.

B.S. 2690 : 1956 Methods of testing water used in industry. British Standards Institution.

ASTM Special technical publication No. 148-D. Manual on industrial water and industrial waste water, 2 Ed 1959. American Society for Testing and Materials.

Standard methods for the examination of water, sewage, and industrial wastes. 1955. American Public Health Association; American Water Works Association; Federation of Sewage and Industrial Wastes Association; New York.

Approved methods for physical and chemical examination of water. 1953. The Institution of Water Engineers; The Royal Institute of Chemistry; The Society of Public Analysts and Other Analytical Chemists; London.

0.6 For particle size IS Sieves (conforming to IS : 460-1962*) have been prescribed. Where IS Sieves are not available, other equivalent test sieves as judged from aperture size may be used.

0.7 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960†.

1. SCOPE

1.1 This standard prescribes the methods of sampling and test (physical and chemical) for water used in industry. It does not include methods of test specifically applicable to highly contaminated waters, such as sea water, sewage and industrial effluents.

1.1.1 Should any inconsistency exist between the methods of test given in this standard and those given in standards for individual materials, the latter shall prevail.

1.1.2 Changes in the methods of sampling which may be necessary in these procedures under specific circumstances may be made in any particular case by mutual agreement of the parties concerned.

2. SAMPLING

2.1 General Requirements of Sampling

2.1.1 Precautions shall be taken to protect the samples, the material being sampled, the sampling instrument and the containers for samples from adventitious contamination.

*Specification for test sieves (*revised*).

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

2.1.2 Samples shall be of sufficient volume and shall be taken frequently enough to permit an accuracy of testing requisite for the desired objective.

2.1.3 Samples shall be collected, packed, transported and manipulated prior to analysis in a manner that safeguards against change in the particular constituents or properties to be examined.

2.1.4 While submitting samples, the information given in Appendix A shall be supplied.

2.2 Apparatus

2.2.1 The apparatus, such as valves, sample lines, sample coolers, degassers, etc, depends on a variety of factors and shall, therefore, be subject to agreement between the parties.

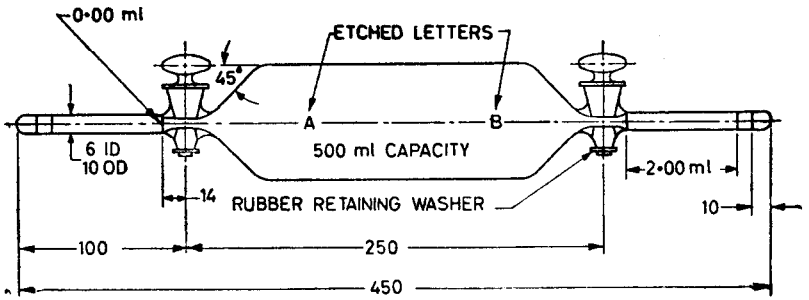
2.2.2 *Sample Containers*

2.2.2.1 Sample containers shall be made of chemically-resistant glass. Before use, they shall be cleaned thoroughly to remove all extraneous surface dirt. Soda-lime glass bottles are not recommended as sample containers; however, if properly coated with paraffin wax, such bottles are suitable for collection and storage of industrial water for most of the tests.

NOTE — New chemically-resistant glass containers shall be aged by allowing them to stand full of distilled water for several days. Ageing may be hastened by a preliminary treatment with dilute sodium hydroxide solution. Samples for residual chlorine determination should be suitably protected against action of direct light.

2.2.2.2 The closures for the sample containers shall be glass stoppers, new cork stoppers that have been thoroughly washed or plastic caps with suitable liners.

2.2.3 When contact with air causes a change in the concentration of a constituent to be determined, such as ammonia, free carbon dioxide, oxygen and sulphur dioxide, the sampling bottle made of glass and shown in Fig. 1 is suitable.



All dimensions are approximate and in millimetres.

FIG. 1 SAMPLING BOTTLE FOR UNSTABLE CONSTITUENTS

2.3 Frequency of Sampling — A reasonably accurate estimate of the composition of a raw water piped from a large body of water far enough from the shoreline to avoid variation from inflowing tributaries and sewage contamination, may be made by taking individual samples at infrequent intervals, such as biweekly or monthly. If samples are taken from near the shoreline of such a body of water or from a river, they may be taken at shorter intervals, for instance daily. Where greater variations occur or closer control in plant intake water is required, samples may be collected more frequently, for example, at hourly intervals.

2.4 Number of Samples

2.4.1 Samples for unstable constituents listed in **2.2.3** shall be obtained in individual containers. Variations of these constituents may be determined by analysis of the individual samples.

2.4.2 For the other tests, composite sample may be made by mutual agreement of the parties by combining individual samples taken at frequent intervals or by means of an automatic sampler. In either case, it shall be indicated if the volume of the sample is proportional to the rates of flow. At the end of a definite period, the composite sample shall be mixed thoroughly.

2.4.3 When samples are taken from a stream, composite sample for analysis shall normally consist of equal quantities of daily samples for a suitable number of consecutive days, for example, seven days.

2.5 Temperature Adjustment of Samples — Where samples of water are taken at other than ambient temperatures, suitable cooling coils shall be used to adjust the sample approximately to the ambient temperatures. Some test methods require adjustment of sample to other than ambient temperatures; such temperature adjustments shall be carried out.

2.6 Suspended Solids

2.6.1 Normally samples are secured without separation of suspended solids. Where constituents are present in colloidal and flocculent suspension, the sample shall be taken so that they are present in representative proportion.

2.6.2 If it is desired to secure samples free of suspended solids from water at an elevated temperature, a filter shall be incorporated in a by-pass line to the cooling coil and the sample taken through this filter.

2.7 Volume of Sample — A minimum of 4 litres of the sample shall be furnished for the analysis, though in some cases a sample as large as 20 litres may be necessary. The number of tests to be made and the amount required for each test shall determine the size of the sample above the minimum specified above.

2.8 Point of Sampling

2.8.1 In those cases where the industrial water available at a particular specific point is to be tested, the question of choosing the point of sampling does not arise. However, in those cases where the quality of a particular supply of water, for example, a stream or lake, is to be ascertained the procedure given below in choosing the point of sampling shall be followed.

2.8.2 The point of sampling shall be chosen with extreme care so that a representative sample of water to be tested is obtained.

2.8.2.1 Because of a wide variety of conditions found in streams, lakes, reservoirs, and other bodies of water, it is not possible to prescribe the exact point of sampling. Where the water in a stream is mixed so as to approach uniformity, a sample taken at any point in the cross-section is satisfactory. For large rivers or for streams not likely to be uniformly mixed, three or more samples are desirable and are usually taken at the mid-point of equal cross-sectional areas. Ordinarily, samples are taken at these points and then combined to obtain an integrated sample of such a stream of water.

2.8.2.2 Choose the location of the sampling point with respect to the information desired and in conformity to local conditions. Allow sufficient distance down-stream with respect to stream flow at the time of sampling from a tributary or source of industrial or sewage pollution to permit thorough mixing. If this is not possible, it is better to sample the stream above the tributary or source of pollution and in addition, to sample the tributary or source of pollution. In general, a distance of one and a half to five kilometres below the tributary is sufficient.

2.8.2.3 Collect samples at least one kilometre below dams or water-falls to allow time for the escape of entrained air. Where lakes, reservoirs, or other bodies of water are sampled, sufficient distance shall be allowed to eliminate the influence of local conditions.

2.8.2.4 It is desirable to take a series of samples from any source of water to determine whether differences in composition are likely to exist, before final selection of the sampling point.

2.8.2.5 In taking samples from open wells, it is best to lower the sampling bottle rather rapidly under the surface of water and to take the sample from about 30 cm below the surface.

2.8.2.6 Choose sampling points in pipelines, conduits, tanks, vats, filters, zeolite and chemical water softeners, de-ionizing processes, surface condensers, evaporators, or condensate return lines with respect to the characteristics of the individual piece of equipment containing the water to be tested, the character and changes occurring between the inlet and outlet water, and rate of passage through the equipment. Again take care that a representative sample is ensured by allowing mixing to take place.

Avoid taking the sample along the wall of the pipe or conduit but take it within the stream.

2.8.2.7 Insert nozzles to sampling cocks into the pipeline or piece of equipment to such a depth as to prevent pipe surface sampling. Choose a point along the length of the pipe where there is minimum disturbance of flow due to fittings.

2.9 Preparation of Samples

2.9.1 Regulate the rate of flow to not more than 500 ml per minute, after first flushing the sample line at a rate high enough to remove all sediment and gas pockets. In special cases where dissolved gases are released from solution by the drop in pressure, note this in the information supplied with the sample (*see* Appendix A).

2.9.2 When sampling water from cocks or valves, insert the sample line, or a thoroughly washed glass or sulphur-free rubber tube extension of the sample line, into the sampling bottle so that it touches the bottom. Allow a volume of water equal to at least ten times the volume of the sample container to flow into and overflow from the container before the sample is taken.

2.9.3 Where contact with air would cause a change in the concentration of a constituent to be determined, the sample shall be taken out of contact with air. As stated in **2.2.3**, for such purposes the apparatus shown in Fig. 1 is suitable. For actual collection of sample with such apparatus, two sampling tubes are arranged so that the tubes are vertical, with their upper outlets free of hose connections and at a higher level than the valve for adjustment of sample flow. Connect the lower ends to the sampling line by means of rubber tubing and a Y-tube. If the water being sampled is above room temperature, the sampling line shall contain a suitable cooling coil. The valve for adjusting the flow of the sample shall be at the outlet from the cooling coil. The sample flow shall be adjusted to a rate that will fill the two tubes simultaneously in 40 to 60 seconds. Continue this flow long enough to provide at least ten changes of water in the sampling tubes. Close the upper stopcocks of the two tubes simultaneously and immediately close the two lower stopcocks and remove the tubing connections. Invert and examine both tubes to ensure the absence of any gas bubbles. If any bubbles are discovered, discard both samples and collect new ones.

2.9.4 For sampling of unconfined waters at any specific depth in streams, lakes, reservoirs, and other bodies of water where contact with air or agitation of the water would cause a change in concentration of a constituent to be determined, use a sampling apparatus so constructed that the water at the depth to be sampled flows through a tube to the bottom of the container, and that a volume of water equal to four to ten times the

volume of the receiving container passes through it. When no determinations of dissolved gases are made, any less complicated apparatus may be used that will permit the collection of a sample at a desired depth, or of an integrated sample containing water from all points in a vertical section.

2.10 Preservation of Samples — Chemical preservatives shall be added only as specified in specific test methods.

2.11 Time Interval Between Collection and Analysis of Samples

2.11.1 In general, allow as short a time as possible to elapse between the collection of a sample and its analysis. Under some conditions, analysis in the field is necessary to secure reliable results. The actual time which may be allowed to intervene between the collection and analysis of a sample varies with the type of examination to be conducted, the character of the sample, and the time interval allowable for applying corrective treatment.

2.11.2 On the statement of an analysis, specify the length of time elapsed between collection and analysis of the sample.

2.11.3 Make the determination of dissolved gases, for instance, oxygen, hydrogen sulphide, carbon dioxide and residual chlorine at the source and immediately after collection; except that in some cases such constituents may be fixed and determined later as specified in specific test methods.

3. GENERAL PRECAUTIONS AND DIRECTIONS FOR TESTS

3.1 Quality of Reagents — Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1960*) shall be used in tests.

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

3.2 It is important that a representative sample is obtained. Appropriate methods of sampling are given in **2**. However, in tests where specific sampling procedures are prescribed, these shall be followed.

3.3 Many analytical procedures given are subject to interference from other constituents that may be present. Whenever interference is encountered or suspected, and no specific procedure is laid down for overcoming it, steps shall be taken to eliminate the interference without adversely affecting the analysis itself.

3.4 Except where otherwise specified, before carrying out a determination, the sample shall be filtered to obtain a clear filtrate. For some tests, for example, for free carbon dioxide, filtration is not permissible. In such

*Specification for water, distilled quality (*revised*).

cases, the sample may be allowed to stand for some time to allow the suspended matter to settle.

3.5 Where the range of amount of the substance being determined is stated, it is usually given in either micrograms (μg) or milligrams. The procedures laid down for the various tests cover the stated ranges, but may, if necessary, be modified either by taking a smaller volume of the sample and diluting with distilled water or in other cases by taking a larger volume of the sample and evaporating it.

3.6 For determinations for which calibrated glass discs are available, these may be used for routine examination provided instructions of the manufacturer are followed. But in case of dispute, test methods as prescribed in this standard shall be followed.

4. GENERAL APPEARANCE

4.1 A brief description of the general appearance of the sample, such as colourless, clear, sparkling, hazy, etc, when drawn and when received in the laboratory shall be recorded.

4.1.1 Samples containing dissolved iron may become turbid subsequent to collection, and if this occurs, it shall also be recorded.

5. COLOUR

5.0 Outline of the Method — The colour of the sample is matched against a series of standards containing potassium chloroplatinate and cobalt chloride.

5.1 Terminology — For the purpose of this test, the following definitions shall apply.

5.1.1 *True Colour* — colour due to substances in solution, after removal of suspended matter.

5.1.2 *Apparent Colour* — colour due to substances which are in solution as well as in suspension.

5.1.3 *Hazen Unit* — colour obtained in a mixture containing either one milligram of platinum or 2·49 mg of potassium chloroplatinate along with 2 mg of cobalt chloride ($CoCl_2.6H_2O$) in 1 litre of the solution.

5.2 Apparatus

5.2.1 *Nessler Tubes* — flat-bottom tubes of thin colourless glass. Two types of tubes are required. The longer tubes shall be 45 cm tall and 2·5 cm in internal diameter. The shorter tubes shall be 30 cm tall and 1·7 cm in internal diameter. Tubes of any one type shall be identical in

shape, and the depth measured internally from the graduation mark to the bottom shall not vary by more than 2 mm in the tubes used.

5.3 Reagents

5.3.1 *Platinum or Potassium Chloroplatinate*

5.3.2 *Aqua Regia* — prepared by mixing one part by volume of concentrated nitric acid (conforming to IS : 264-1950*) with three parts by volume of concentrated hydrochloric acid (conforming to IS : 265-1962 †).

5.3.3 *Cobalt Chloride* — crystalline, with the molecular composition $CoCl_2.6H_2O$.

5.4 Procedure

5.4.1 *Preparation of Colour Standards* — Dissolve 0·500 g of metallic platinum in *aqua regia* and remove nitric acid by repeated evaporation to dryness on water-bath after addition of excess of concentrated hydrochloric acid (conforming to IS : 265-1962†). Dissolve the residue with 1·0 g of cobalt chloride in 100 ml of concentrated hydrochloric acid to obtain a bright solution, if necessary by warming. Dilute the solution to 1 000 ml with distilled water. This stock solution has a colour of 500 Hazen units. A more convenient way of preparing the same solution is by dissolving 1·245 g of potassium chloroplatinate and 1·0 g of cobalt chloride in distilled water and diluting to 1 litre.

5.4.1.1 Prepare a set of colour standards having colour of 5, 10, 15, 20, 25, 30, 35, 40, 50, 60 and 70 Hazen units by diluting the stock solution with water. Protect these colour standards from evaporation and contamination when not in use.

5.4.1.2 The colour standards shall be freshly prepared for each determination. But in routine practice, they may be used repeatedly, provided they are protected against evaporation and contamination when not in use.

5.4.2 *Procedure for Clear Samples* — For samples having turbidity (*see* **6**) under 5 mg/l, match the colour of the sample against the standard colours in the longer Nessler tubes (*see* **5.2.1**). Fill the tubes to mark and compare the colour by looking vertically downwards against a pure white surface. If the colour is found to exceed 70 units, dilute the sample with distilled water before comparison and multiply the result by appropriate factor.

5.4.2.1 As matching is very difficult when the colour of the sample is below 5 Hazen units, report the colour as ' less than 5 Hazen units ' in such cases.

*Specification for nitric acid.

†Specification for hydrochloric acid (*revised*).

5.4.2.2 When the colour of the sample exceeds 30 Hazen units, the comparison may, if desired, be made in the shorter Nessler tubes.

5.4.3 *Procedure for Turbid Samples* — If the sample has turbidity over 5 mg/l, it becomes impossible to measure the true colour accurately by the method prescribed in **5.4.2** and if an attempt is made, the value found shall be reported as 'apparent colour'. In the presence of turbidity, the true colour shall be determined after centrifuging. The sample shall be centrifuged until the supernatant liquid is clear. The centrifuged clear sample shall be compared by the method prescribed in **5.4.2.**

NOTE — For estimating true colour, filter paper shall not be used since that leads to erroneous results.

5.5 Report — The results of colour determination shall be expressed in whole numbers and shall be recorded as follows:

Hazen Units			
Less than 5	Report as 'Less than 5 Hazen units'		
5 to 50	Report to the nearest 1 Hazen unit		
51 to 100	do	5	do
101 to 250	do	10	do
251 to 500	do	20	do

NOTE — The colour determination shall be made as early as possible after the collection of samples as certain biological changes occurring in storage may affect the colour.

6. TURBIDITY

6.0 Outline of the Method — The sample is matched against standard suspensions of fullers' earth in water.

6.1 Terminology — For the purpose of this test, the following definition shall apply.

6.1.1 *Silica Scale Unit* — turbidity imparted by 1 mg of fullers' earth when suspended in 1 000 ml of distilled water.

6.2 Preparation of Turbidity Standards — Mix slowly with constant stirring 5·000 g of fullers' earth previously dried and sifted through 75-micron IS Sieve with distilled water and dilute it to 1 000 ml. Agitate intermittently for one hour and then allow to stand for 24 hours. Withdraw the supernatant liquid without disturbing the sediment. Evaporate about 50 ml of the removed liquid, dry the residue at 105° ± 2°C and weigh the residue to determine the amount of clay in suspension. Prepare turbidity standards with this standardized stock suspension with distilled

water. A drop of saturated mercuric chloride solution may be added as preservative. The standards are stable for three months.

6.3 Procedure — Pour the sample after thorough shaking into a clear glass bottle of suitable capacity, say, one litre. Compare it with the turbidity standards contained in similar bottles, holding them against a suitable background and using a source of light which illuminates them equally and is placed so that no rays reach the eye directly. The sample and the standards shall be shaken simultaneously immediately before comparison. If the sample has turbidity over 100 units, dilute it with distilled water before testing and multiply the result with an appropriate factor.

NOTE — Comparison of turbidity may also be done with the help of suitable instruments.

6.3.1 *Report* — Record the turbidity readings in accordance with Table 1.

TABLE 1 RECORDING OF TURBIDITY READINGS

SL No.	TURBIDITY (SILICA SCALE UNITS)		RECORD TO THE NEAREST (UNITS)
	Greater than	Up to	
(1)	(2)	(3)	(4)
i)	0·0	1·0	0·1
ii)	1	10	1
iii)	10	100	5
iv)	100	400	10
v)	400	700	50
vi)	700	—	100

7. ODOUR

7.0 General — Odour of water, though very important, cannot be determined in absolute units. Olfactory sense which is the most sensitive means of detecting small concentration of odoriferous substances lacks precision and mathematical expression. In case of doubt as to the intensity or character of odour, a majority opinion of several observers should be recorded.

7.1 Preparation of Apparatus — Thoroughly clean the required number of wide-mouth glass-stoppered bottles of about one litre capacity. Rinse them

with hydrochloric acid and render them completely odourless by repeated washing with odour-free distilled water, which can be prepared by passing distilled water through a column of granulated activated carbon.

7.2 Procedure — As soon as possible after collection of sample, fill a bottle (cleaned as in **7.1**) half-full of sample, insert the stopper, shake vigorously for 2 to 3 seconds and then quickly observe the odour. The sample taken for observation of odour shall be at room temperature.

7.2.1 When it is desired to record the odour at an elevated temperature, make the observation after warming the sample in a clean stoppered bottle to about 60°C.

8. *p*H VALUE (HYDROGEN ION CONCENTRATION)

8.0 Methods — The determination shall be carried out either by the electrometric method or the indicator method. In case of dispute, the electrometric method shall be considered as the referee method.

NOTE — Resistant glass bottles shall be used for the sample and this test shall be done as soon as possible after the sample is drawn. Samples kept for a long time are likely to change in *p*H due to escape of dissolved gases, such as carbon dioxide.

8.1 Electrometric Method — The determination may be made by any *p*H meter with glass electrode.

8.2 Indicator Method

8.2.1 *Reagents* — A series of indicators and buffer solutions are required for this method. Methods of preparation of these solutions are given in Appendix B.

8.2.2 *Procedure* — Take 100 ml of the sample in a hard glass tube and determine the approximate *p*H by using a universal indicator. Repeat using a solution of the indicator (about 1/20 of the volume of the liquid being tested) which corresponds to the approximate *p*H found above. Compare the colour produced with a series of buffer solutions of known *p*H, each containing the same proportion of the indicator. Report as *p*H, the *p*H of the buffer solution which matches with that of the sample.

9. ELECTRICAL CONDUCTANCE

9.0 General — The unit of conductance is the mho or reciprocal ohm. Specific conductivity is the conductance at a specified temperature across a column of a liquid 1 cm^2 in area and 1 cm long, and is expressed in mhos per centimetre. This is an inconveniently large unit for water testing and it is usual to use the micromho per centimetre known as the ' dionic unit ', which is one-millionth part of a mho per centimetre.

9.1 Apparatus — Several kinds of apparatus are available. They generally consist of two parts.

9.1.1 *Conductivity Cell* — containing a pair of electrodes. The sample to be tested is poured into this cell. There are many forms of cell. One of the most convenient types is provided with a funnel for filling, a drain for emptying, and an overflow for maintaining constant level. Electrodes for use with samples having very low dissolved solids (such as condensates) should not be coated with platinum black. Platinum black which has been heated to redness until it is grey is suitable. Bright platinum or gold or heavily gold plated electrodes may be used.

9.1.1.1 Some instruments are designed to work with a particular form of conductivity cell, and are then calibrated directly in conductivity units. Other instruments, primarily introduced for more general application, are calibrated on conductance units and their readings require multiplication by a factor known as the ' cell constant ' which shall be determined by experiment.

9.1.2 *Measuring Instrument* — for measuring the electrical conductance (or the resistance which is the inverse of conductance) between the electrodes of the cell. There are several satisfactory commercial models. Operators, unless they have adequate facilities, would be well advised to purchase a ready-made instrument.

9.2 Procedure

9.2.1 Determine the cell constant if necessary, either directly with a standard potassium chloride solution (say 0·002 N) or by comparison with a cell the constant of which is known accurately. (In the latter case, the concentration and nature of the electrolytes in the liquid which is used for the comparison should be the same and should be similar respectively to those of the liquids with which the cell is likely to be used in practice.)

9.2.2 Use some of the sample to wash out the conductivity cell thoroughly. Fill the conductivity cell with the sample. Measure the conductivity in accordance with the instructions of the instrument manufacturer.

9.3 Calculation

9.3.1 *For Instrument Reading Resistance*

$$\text{Electrical conductance, in dionic units (or micromhos per centimetre)} = \frac{1}{rk} \times 10^6$$

where

r = resistance in ohms, and

k = cell constant.

9.3.2 *For Instrument Reading Conductance*

Electrical conductance, in dionic units (or micromhos per centimetre) = ck

where

c = conductance in micromhos, and

k = cell constant.

9.4 Correlation of Electrical Conductance to Total Dissolved Solids — 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

$$\frac{\text{Electrical conductance}}{\text{Dissolved solids}}$$

for a particular series of samples.

10. TOTAL SOLIDS

10.1 Procedure

10.1.1 Heat a clean and dry platinum dish of about 100 ml capacity to redness and cool it in a desiccator. Weigh the dish. Alternatively, a nickel or silica dish may be used, in which case dry it at about 105°C for 30 minutes and then cool it to room temperature.

10.1.2 Pipette out 100 ml (or 250 ml for samples of low salinity) of the well-mixed sample in stages into the weighed dish, and evaporate to dryness on a steam-bath. Wipe the outside of the dish and dry the residue for one hour at 103° to 105°C. Transfer the dish to a desiccator and weigh it as soon as room temperature is reached. Repeat drying and weighing till the weight is constant to within 0·5 mg. Reserve the residue for test in **11.1**. Express the result to nearest 5 mg/l.

10.2 Calculation

$$\text{Total solids, mg/l} = \frac{W \times 10^6}{v}$$

where

W = weight in g of residue obtained, and

v = volume in ml of the sample taken.

11. IGNITED RESIDUE

11.1 Procedure — Ignite the residue reserved in **10.1.2** at 525° to 550°C for 30 minutes. Weigh the ignited residue after cooling it in a desiccator to room temperature.

NOTE — If there is any odour or change of colour during ignition, include it in the report.

11.2 Calculation

$$\text{Ignited residue, mg/l} = \frac{W \times 10^6}{v}$$

where

W = weight in g of the ignited residue, and
v = volume in ml of the sample taken in **10.1.2.**

12. SUSPENDED MATTER AND TOTAL DISSOLVED SOLIDS

12.0 General — For determining suspended matter and total dissolved solids, the following procedure shall be adopted.

12.0.1 Where the suspended matter is high, the same shall be determined by the method given in **12.1** and total dissolved solids shall be found by subtracting the suspended matter (as mg/l) from total solids (as mg/l).

12.0.2 When the suspended matter is low, the sample shall be filtered through a filter paper and the total dissolved solids determined in the filtrate by a procedure of evaporation given in **10.1.** Suspended matter shall then be obtained by subtracting total dissolved solids (as mg/l) from total solids (as mg/l).

12.1 Determination of Suspended Matter

12.1.1 *Procedure* — Take a Gooch crucible with aperture 0·3 to 0·5 mm. Pour into it 20 to 30 ml of a 0·5 percent suspension of Gooch asbestos in water. Let it drain for a couple of minutes, then apply gentle suction followed by hard suction. Wash with distilled water, dry first at low temperature and finally ignite strongly. Allow to cool and re-wash with distilled water using strong suction. Dry at 103° to 105°C until weight is constant. Filter a known volume of the sample through the Gooch crucible. After filtration, wash with distilled water. Dry at 103° to 105°C for one hour. Cool and weigh.

12.1.2 *Calculation*

$$\text{Suspended matter, mg/l} = \frac{W \times 10^6}{v}$$

where

W = weight in g of the suspended matter, and

v = volume in ml of the sample taken for filtration.

13. TOTAL ALKALINITY

13.0 Outline of the Method — The sample is titrated against standard acid using methyl orange indicator.

13.1 Reagents

13.1.1 *Standard Hydrochloric Acid* — 0·02 N.

13.1.2 *Methyl Orange Indicator* — Dissolve 0·1 g of methyl orange in distilled water and dilute to 1 litre.

13.2 Procedure — Titrate over a white surface 100 ml of the sample contained in a 250-ml conical flask with standard hydrochloric acid using two or three drops of methyl orange indicator.

NOTE — If more than 30 ml of acid is required for the titration, a smaller suitable aliquot of the sample shall be taken.

13.3 Calculation

$$\text{Total alkalinity (as } CaCO_3\text{), mg/l} = 10\ V$$

where

V = volume in ml of standard hydrochloric acid used in the titration.

13.4 Precision and Accuracy — A precision of ± 1 mg/l and an accuracy of ± 2 mg/l, expressed as $CaCO_3$, are achieved in the range 10 to 500 mg/l.

14. ALKALINITY TO PHENOLPHTHALEIN

14.0 Outline of the Method — The sample is titrated against standard acid using phenolphthalein indicator.

14.1 Reagents

14.1.1 *Phenolphthalein Indicator Solution* — Dissolve 0·1 g of phenolphthalein in 60 ml of rectified spirit conforming to IS : 323-1959* and dilute with distilled water to 100 ml.

14.1.2 *Standard Hydrochloric Acid* — 0·02 N.

14.2 Procedure — Add 2 drops of phenolphthalein indicator solution to a sample of suitable size, 50 or 100 ml, in a conical flask and titrate over a white surface with standard hydrochloric acid.

14.3 Calculation

$$\text{Alkalinity to phenolphthalein (as } CaCO_3\text{), mg/l} = \frac{1\,000\ V_1}{V_2}$$

*Specification for rectified spirit (*revised*).

where

V_1 = volume in ml of standard hydrochloric acid used in the titration, and

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

14.4 Precision and Accuracy — A precision of ± 1 mg/l and an accuracy of ± 2 mg/l, expressed as $CaCO_3$, are achieved in the range 10 to 500 mg/l.

15. CAUSTIC ALKALINITY

15.0 General — Caustic alkalinity is the alkalinity corresponding to the hydroxides present in water and is calculated from total alkalinity (T) and alkalinity to phenolphthalein (P).

15.1 Procedure — Determine total alkalinity as in **13.2** and alkalinity to phenolphthalein as in **14.2** and calculate caustic alkalinity as shown in Table 2.

TABLE 2 CALCULATION OF CAUSTIC ALKALINITY FROM TOTAL ALKALINITY (T) AND ALKALINITY TO PHENOLPHTHALEIN (P)

VALUE OF P AND T	CAUSTIC ALKALINITY
(1)	(2)
$P = 0$	0
$P < \frac{1}{2} T$	0
$P = \frac{1}{2} T$	0
$P > \frac{1}{2} T$	$2P - T$
$P = T$	T

16. TOTAL HARDNESS

16.0 General

16.0.1 Total hardness of water is the sum of the concentrations of all the metallic cations other than cations of the alkali metals, expressed as equivalent calcium carbonate concentration. In most waters, nearly all of the hardness is due to calcium and magnesium ions, but in some waters, measurable concentrations of iron, aluminium, manganese, zinc and other metals have to be taken into consideration.

16.0.2 Two methods are prescribed for determining total hardness. The method prescribed in **16.1** is based on the reaction of calcium and

magnesium salts with sodium ethylenediamine tetra-acetate (EDTA). The method prescribed in **16.2** is based on computation from analytical results of the sample. In case of dispute, the method given in **16.2** shall be used.

16.1 EDTA Method

16.1.1 *Reagents*

16.1.1.1 *Indicator solution A* — Dissolve 0·5 g of eriochrome black *T* in 100 ml of triethanolamine.

16.1.1.2 *Buffer solution A* — (a) Dissolve 40 g of borax in approximately 800 ml of distilled water. (b) Dissolve 10 g of sodium hydroxide, 10 g of sodium potassium tartrate and 5 g of sodium sulphide in 100 ml of distilled water. When cool, mix the two solutions and dilute to 1 000 ml with distilled water. The reagent should not be used more than one month after preparation.

16.1.1.3 *Standard calcium chloride solution* — Dissolve 1·000 g of calcium carbonate, contained in a beaker covered with a watch-glass, in a small quantity of dilute hydrochloric acid. Wash down the beaker and watch-glass with carbon dioxide-free distilled water, neutralize exactly with sodium hydroxide solution and make up to 1 000 ml with carbon dioxide-free distilled water. One millilitre of the solution is equivalent to 1 mg of calcium carbonate.

16.1.1.4 *EDTA solution* — Dissolve 4·0 g of disodium ethylenediamine tetra-acetate dihydrate in approximately 800 ml of distilled water. Add 0·86 g of sodium hydroxide (21·5 ml of 1 N solution) and 0·1 g of magnesium chloride ($MgCl_2.6H_2O$). Titrate against standard calcium chloride solution (10 ml diluted to 50 ml) as described in **16.1.2** and adjust so that 1 ml is equivalent to 1 mg of calcium carbonate.

16.1.1.5 *Indicator solution B* — Dissolve 0·5 g of eriochrome black T and 4·5 g of hydroxylamine hydrochloride in 100 ml of rectified spirit.

16.1.1.6 *Buffer solution B* — Dissolve 67·5 g of ammonium chloride in 570 ml of ammonium hydroxide (sp gr 0·92) and dilute to 950 ml with distilled water. Dissolve 0·616 g of magnesium sulphate ($MgSO_4.7H_2O$) and 0·93 g of disodium ethylenediamine tetra-acetate dihydrate in 50 ml of distilled water and add to the ammonium hydroxide-chloride mixture.

16.1.2 *Procedure* — Measure 50 ml of the sample into a 250-ml conical flask. Add 4 to 6 drops of indicator solution A and mix; add 0·5 ml of buffer solution A and mix. Titrate immediately with EDTA solution with continuous mixing until the colour changes from red to blue. As the end point is approached, the solution shows some blue colouration but a definite reddish tinge is observed and is discharged at the end point.

NOTE 1 — To avoid overtitrating, it is suggested that 40 to 45 ml of the sample be titrated approximately to the end point, and then the remainder of the sample added and the titration continued carefully to the final end point.

NOTE 2 — It is recommended that for hardness below 100 mg/l, 100 ml of the sample be used with 7 to 9 drops of indicator solution A and 1·0 ml of buffer solution A, whereas for hardness appreciably above 200 mg/l, a smaller volume than 50 ml of the sample be taken and diluted to 50 ml with distilled water. For samples of very low hardness, take 500 ml of the sample. Add 6 drops of indicator solution B and 2 ml of buffer solution B. Titrate as above.

16.1.3 *Calculation* — Calculate as follows and express the result to the nearest 5 mg/l:

$$\text{Total hardness (as } CaCO_3\text{), mg/l} = \frac{1\,000V_1}{V_2}$$

where

V_1 = volume in ml of the EDTA solution used in the titration, and

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

16.1.4 *Precision and Accuracy* — The EDTA method is applicable in the range 0·1 to 25 mg in terms of calcium carbonate. The precision is within 1 mg/l. The accuracy depends on the interfering substances present. In the absence of any interference, it is within 1 mg/l.

16.2 Method Based on Analytical Data

16.2.1 In this case, total hardness shall be computed from the concentrations of the different metallic cations (other than alkali metals) in the sample but most often the cations taken into account are calcium, magnesium, iron, aluminium, zinc and manganese.

16.2.2 *Calculation*

$$\begin{aligned}\text{Total hardness (as } CaCO_3\text{), mg/l} = {} & (2{\cdot}497 \times \text{mg/l Ca}) \\ & + (4{\cdot}116 \times \text{mg/l Mg}) \\ & + (2{\cdot}69 \times \text{mg/l Fe}) \\ & + (5{\cdot}567 \times \text{mg/l Al}) \\ & + (1{\cdot}531 \times \text{mg/l Zn}) \\ & + (1{\cdot}822 \times \text{mg/l Mn})\end{aligned}$$

16.3 Expression of Values of Hardness in Different Units — Hardness of water shall be expressed in terms of mg/l of calcium carbonate. However, for the sake of convenience, factors for converting the value of hardness into different units that are in use are given in Table 3.

17. CARBONATE HARDNESS AND NON-CARBONATE HARDNESS

17.0 General

17.0.1 *Carbonate Hardness* — is the hardness caused by the carbonates and bicarbonates of metals other than alkali metals.

TABLE 3 CONVERSION FACTORS FOR DIFFERENT UNITS FOR EXPRESSING HARDNESS

(*Clause* 16.3)

Sl No.	Unit of Hardness	mg/l (as $CaCO_3$)	British Degree, Grains per Imperial Gallon (as $CaCO_3$)	American Degree, Grains per US Gallon (as $CaCO_3$)	French Degree, Parts per 100 000 (as $CaCO_3$)	German Degree, Parts per 100 000 (as CaO)	Russian Degree, Parts per Million (as Ca)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
i)	mg/l as $CaCO_3$	1·00	0·07	0·058	0·10	0·056	0·40
ii)	British degree	14·29	1·00	0·83	1·43	0·79	5·72
iii)	American degree	17·16	1·20	1·00	1·72	0·96	6·86
iv)	French degree	10·00	0·70	0·58	1·00	0·56	4·00
v)	German degree	17·86	1·25	1·04	1·79	1·00	7·14
vi)	Russian degree	2·50	0·18	0·15	0·25	0·14	1·00

17.0.2 *Non-carbonate Hardness* — is the hardness caused by salts other than carbonates and bicarbonates of metals other than alkali metals.

17.1 Procedure — Determine the total alkalinity as in **13.2** and total hardness as in **16** and calculate as given in **17.2.**

17.2 Calculation

17.2.1 *Carbonate Hardness*

a) When total hardness is greater than total alkalinity, carbonate hardness (as $CaCO_3$ mg/l) is equal to total alkalinity (as $CaCO_3$).

b) When total hardness is equal to or less than total alkalinity, carbonate hardness (as $CaCO_3$ mg/l) is equal to total hardness (as $CaCO_3$).

17.2.2 *Non-carbonate Hardness*

Non-carbonate hardness (as $CaCO_3$), mg/l = total hardness — total alkalinity

18. EXCESS ALKALINITY

18.0 General — Excess alkalinity is the alkalinity, in terms of sodium carbonate, equal to the excess of total alkalinity over total hardness.

18.1 Procedure — Determine the total alkalinity as in **13.2** and total hardness as in **16.**

18.2 Calculation — Calculate excess alkalinity as below and express the result to the nearest 5 mg/l:

Excess alkalinity (as Na_2CO_3), mg/l = 1·06 [total alkalinity (as $CaCO_3$ mg/l) — total hardness (as $CaCO_3$ mg/l)]

19. TOTAL ACIDITY AND MINERAL ACIDITY

19.0 Outline of the Method — The sample is titrated against standard sodium hydroxide solution, using phenolphthalein indicator for total acidity and methyl orange indicator for mineral acidity.

19.1 Reagents

19.1.1 *Phenolphthalein Indicator Solution* — same as in **14.1.1.**

19.1.2 *Methyl Orange Indicator Solution* — same as in **13.1.2**

19.1.3 *Sodium Hydroxide Stock Solution* — Prepare an approximately 1 N solution of sodium hydroxide by dissolving approximately 20 g of sodium

hydroxide in 500 ml of freshly boiled and cooled distilled water. Determine the normality by titration with a standard solution of an acid.

19.1.4 *Standard Sodium Hydroxide Solution* — Prepare 0·02 N solution by diluting a calculated volume of sodium hydroxide stock solution with distilled water which has been freshly boiled for at least 10 minutes to expel carbon dioxide. Store in a lightly capped polyethylene bottle. This solution shall be prepared fresh every week.

19.2 Procedure

19.2.1 *Total Acidity* — Add 3 drops of phenolphthalein indicator to 100 ml of the sample in a conical flask. Titrate over a white surface with standard sodium hydroxide solution.

19.2.2 *Mineral Acidity* — Add 2 drops of methyl orange indicator to 100 ml of the sample in a conical flask. Titrate over a white surface with standard sodium hydroxide solution.

NOTE 1 — For snarp end point, the volume of the titrant should not be more than 50 ml. If more than 50 ml is required, a suitable aliquot should be taken for the titration.

NOTE 2 — If free residual chlorine is present in the sample, add 0·05 ml (1 drop) of 0·1 N sodium thiosulphate solution.

19.3 Calculation

a) Total acidity (as $CaCO_3$), $mg/l = \frac{1\,000\,V_1}{V_2}$

b) Mineral acidity (as $CaCO_3$), $mg/l = \frac{1\,000\,V_3}{V_2}$

where

V_1 = volume in ml of standard sodium hydroxide solution used in **19.2.1**,

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

V_3 = volume in ml of standard sodium hydroxide solution used in **19.2.2**.

19.4 Precision and Accuracy — In the absence of iron and aluminium, the method has an estimated precision of ± 2 mg/l and an accuracy of about ± 4 mg/l in the range above 10 mg/l.

20. SULPHATES

20.0 Two methods are prescribed for the determination of sulphates. The gravimetric method given in **20.1** shall be the referee method but for routine analysis, the EDTA method given in **20.2** may be used.

20.1 Gravimetric Method

20.1.0 *Outline of the Method* — Sulphates in the sample are precipitated by barium chloride and the precipitate weighed as barium sulphate.

20.1.1 *Reagents*

20.1.1.1 *Concentrated hydrochloric acid* — conforming to IS : 265-1962*.

20.1.1.2 *Barium chloride solution* — approximately 10 percent *w/v*.

20.1.2 *Procedure* — Add concentrated hydrochloric acid drop by drop to 100 to 500 ml of the sample (filtered if necessary) contained in a beaker until just acid, add three drops in excess and evaporate to about 50 ml. Filter if necessary and wash the filter paper with distilled water, collecting the washings with the filtrate. Bring the solution to the boil and add boiling barium chloride solution until all the sulphate is precipitated. Avoid excess of barium chloride solution. Digest on a hot water-bath until the precipitate has settled, or preferably keep overnight, filter through a filter paper (Whatman No. 44 or its equivalent) or through a Gooch crucible, and wash with hot distilled water until washings are free from chlorides. Ignite and weigh the precipitate.

20.1.3 *Calculation*

$$\text{Sulphates (as } SO_4\text{), mg/l} = \frac{412\,000\ W}{V}$$

where

W = weight in g of the precipitate, and

V = volume in ml of the sample taken for the test.

20.1.4 *Precision and Accuracy* — The accuracy obtainable is within about 1 mg or 1 percent. The method is suitable up to 200 mg of sulphate (as SO_4).

20.2 EDTA Method

20.2.0 *Outline of the Method* — A measured excess of standard barium chloride solution is added to the sample and the excess barium chloride estimated by titration against EDTA.

20.2.1 *Reagents*

20.2.1.1 *Dilute nitric acid* — approximately 1 N.

20.2.1.2 *Standard barium chloride solution* — Dissolve 2·443 g of barium chloride ($BaCl_2.\ 2H_2O$) in distilled water and dilute to 1 litre. One millilitre of this solution is equivalent to 0·96 mg of sulphate (as SO_4).

*Specification for hydrochloric acid (*revised*).

20.2.1.3 *Buffer solution* — Dissolve 67·5 g of ammonium chloride in 570 ml of ammonium hydroxide (sp gr 0·92) and dilute with distilled water to 1 litre.

20.2.1.4 *Eriochrome black T indicator solution* — Dissolve a small quantity of eriochrome black T in 20 ml of distilled water by shaking or warming, and allow to cool. The solution is stable for several days but preparation of a fresh solution before use is recommended.

20.2.1.5 *Standard EDTA solution* — Dissolve 4·0 g of disodium ethylenediamine tetra-acetate dihydrate in 1 litre of distilled water. Standardize the solution by titration against standard barium chloride solution, using the procedure given in **20.2.2** and adjust the solution so that 1 ml is equivalent to 1 ml of standard barium chloride solution.

20.2.2 *Procedure* — Neutralize 100 ml of the sample with dilute nitric acid, adding a slight excess, and boil to expel carbon dioxide. Add 10 ml, or more if required, of standard barium chloride solution to the boiling solution and allow to cool. Dilute to 200 ml, mix and allow the precipitate to settle. Withdraw 50 ml of the clear supernatant liquid, add 0·5 to 1·0 ml of buffer solution and several drops of indicator solution. Titrate with standard EDTA solution to a blue colour which does not change on addition of further drops of EDTA solution.

20.2.3 *Calculation*

$$\text{Sulphates (as } SO_4\text{), mg/l} = 9{\cdot}6\ (0{\cdot}1A + B - 4C)$$

where

A = total hardness of the sample (as $CaCO_3$ mg/l) as determined in **16**,

B = volume in ml of standard barium chloride solution added in **20.2.2**, and

C = volume in ml of standard EDTA solution required for the titration.

21. SULPHITES

21.0 Outline of the Method — The sample is titrated against standard iodate-iodide solution using starch indicator.

21.1 Reagents

21.1.1 *Dilute Hydrochloric Acid* — Add 200 ml of concentrated hydrochloric acid (conforming to IS : 265-1962*) to 100 ml of distilled water.

21.1.2 *Starch Indicator Solution* — Triturate 5 g of starch and 0·01 g of mercuric iodide with 30 ml of cold distilled water and slowly pour it with

*Specification for hydrochloric acid (*revised*).

constant stirring into 1 litre of boiling distilled water. Boil for 3 minutes Allow to cool and decant off the supernatant clear liquid.

21.1.3 *Standard Iodate-Iodide Solution* — Weigh accurately 0·713 g of potassium iodate and dissolve in about 150 ml of distilled water. Add 7 g of potassium iodide and 0·5 g of sodium bicarbonate; when dissolved, dilute the solution to exactly 1 litre.

21.2 Procedure

21.2.1 Collect the sample by running it to the bottom of a 250-ml bottle but allowing about eight to ten times the volume of the bottle to run to waste before taking the sample. For this test, a filtered sample shall not be used unless suspended matter is present containing interfering substances, for example, iron oxide, in which case, insert a filter in the sampling line.

21.2.2 Measure 2 ml of dilute hydrochloric acid into a 350-ml porcelain basin and pour the whole of the sample into the basin. Now add about 1 ml of starch indicator and, with constant stirring, titrate against standard iodate-iodide solution until a faint blue colour is obtained. Measure the volume of the sample container.

21.3 Calculation

$$\text{Sulphites (as } SO_2\text{), mg/l} = \frac{800\ V_1}{V_2}$$

where

V_1 = volume in ml of standard iodate-iodide solution required, and

V_2 = volume in ml of the sample container.

21.4 Range of Accuracy — The method is suitable in the range 1·25 to 20 mg of sulphites (as SO_2).

22. PHOSPHATES

22.0 General

22.0.1 Colorimetric method for determination of phosphates is prescribed. Visual comparison of colour, though provided for in the test procedure, is not recommended because the colour standards change rather rapidly.

22.0.2 *Outline of the Method* — The sample is neutralized to phenolphthalein and reacted with ammonium molybdate and stannous chloride. The blue colour obtained is matched against that produced with a series of standard phosphate solutions.

22.1 Apparatus — For colour comparison, any one of the following apparatus is required.

22.1.1 *Spectrophotometer* — for use at 690 mμ providing a light path of 1 to 10 cm.

22.1.2 *Filter Photometer* — providing a light path of 1 to 10 cm and equipped with a red filter having maximum transmittance between 600 and 700 mμ.

22.1.3 *Nessler Tubes* — 100 ml capacity.

22.2 Reagents

22.2.1 *Decolorizing Carbon* — analytical grade.

22.2.2 *Phenolphthalein Indicator Solution* — same as in **14.1.1**.

22.2.3 *Dilute Sulphuric Acid* — approximately 4 N.

22.2.4 *Ammonium Molybdate Solution* — Dissolve 25 g of ammonium molybdate in 175 ml of distilled water. In another container, add cautiously to 400 ml of distilled water, 310 ml of concentrated sulphuric acid. Cool, add the molybdate solution to this diluted acid and dilute the whole to 1 litre.

22.2.5 *Stannous Chloride Solution* — Dissolve 2·5 g of a *fresh supply* of stannous chloride ($SnCl_2.2H_2O$) in 10 ml of concentrated hydrochloric acid and dilute to 100 ml with distilled water. Filter if turbid. Store the solution in a cool place in an aspirator bottle having a glass stopcock. A 5-mm thick layer of pure mineral oil shall be floated over the surface of the solution to minimise oxidation. Always drain out a little of the solution out of the stopcock before use.

22.2.6 *Standard Phosphate Solution* — Dissolve 0·716 g of dry potassium dihydrogen phosphate (KH_2PO_4) in 1 litre of distilled water. Dilute 100 ml of the solution to 1 litre. One millilitre of the diluted solution contains 0·05 mg of phosphate (as PO_4).

22.3 Procedure

22.3.1 If the sample is turbid or coloured, add two 0·25 g-portions of decolorizing carbon to 200 ml of the sample in a flask, shaking it vigorously for one minute after each addition. Filter through a dry, medium-texture filter paper.

22.3.2 To a 50 ml sample containing not more than 0·15 mg of phosphate (as PO_4), freed from colour and turbidity as in **22.3.1**, add one drop of phenolphthalein indicator. If a pink colour is obtained, add dilute sulphuric acid dropwise to discharge the colour. Add, with thorough mixing after each addition, 2·0 ml of ammonium molybdate solution and 0·25 ml (5 drops) of stannous chloride solution. The rate of colour development and the intensity of colour depend upon the temperature of the final solution, each 1°C increase producing about one percent increase in colour. Hence

samples, control standards and reagents should be within 2°C of one another and at a temperature between 20° and 30°C. After 10 minutes, but before 15 minutes, using the same specific interval for all determinations, measure the colour photometrically and compare with a calibration curve, using a distilled water blank, or compare visually in Nessler tubes against standards prepared simultaneously. A blank shall always be run on the reagents and distilled water.

22.4 Calculation

$$\text{Phosphates (as } PO_4\text{), mg/l} = \frac{1\,000\ W}{V}$$

where

W = weight in mg of phosphate (as PO_4) as read from the calibration curve or in the control standard solution, and

V = volume in ml of the sample taken for the test in **22.3.2.**

22.5 Precision and Accuracy — Precision of the order of ±0·002 5 mg over the range 0·002 5 to 0·15 mg is obtainable with photo-electric measurement. The precision with visual comparison is poorer and depends on the individual. The accuracy depends on the apparatus.

23. FLUORIDES

23.0 Outline of the Method — The colour (red to yellow with increasing concentration of fluoride) obtained with zirconium alizarin reagent is matched against that produced with a series of standard fluoride solutions.

23.1 Apparatus

23.1.1 *Nessler Tubes* — 100 ml capacity.

23.1.2 *Distillation Apparatus* — The distillation apparatus shall consist of a Claisen flask of 100 ml capacity, a large flask for generating steam and an efficient condenser. The main neck of the Claisen flask shall be fitted with a two-holed rubber stopper through which shall pass a thermometer and a glass tube (for connecting with the steam supply), both the thermometer and the tube extending almost to the bottom of the flask. The side neck of the flask shall be closed with a rubber stopper and the side arm connected with the condenser. Steam shall be generated from water made alkaline with sodium hydroxide. Local overheating of the Claisen flask shall be avoided by use of an asbestos board with a hole which shall fit closely to the lower surface of the flask.

23.2 Reagents

23.2.1 *Sodium Thiosulphate Solution* — approximately 0·1 N.

23.2.2 *Standard Sodium Fluoride Solution* — Dissolve 0·221 g of dry sodium fluoride in distilled water and make up to 1 000 ml. Dilute 100 ml of the solution to 1 000 ml. One millilitre of this diluted solution contains 0·01 mg of fluoride (as F). The solution shall be kept in polyethylene or wax-lined glass bottles.

23.2.3 *Zirconium Alizarin Reagent*

a) Dissolve 0·3 g of zirconium oxychloride ($ZrOCl_2.8H_2O$), or 0·25 g of zirconium oxynitrate [$ZrO(NO_3)_2 . 2H_2O$] in 50 ml of distilled water. Dissolve 0·07 g of alizarin sodium monosulphonate (alizarin S) in another 50 ml quantity of distilled water and add the latter solution slowly to the zirconium solution with continuous stirring. The resulting solution clears on standing for a few minutes.

b) Dilute 112 ml of concentrated hydrochloric acid (conforming to IS : 265-1962*) to 500 ml with distilled water. Also add 37 ml of concentrated sulphuric acid (conforming to IS : 266-1961†) to 400 ml of distilled water and then dilute to 500 ml. Mix the two diluted acids when cool.

c) Dilute the clear zirconium solution prepared in (a) to 1 000 ml with the mixed acid solution prepared in (b). The reagent is at first red, but within an hour it changes to orange-yellow and is ready for use. The solution shall be stored in the dark; if kept in a refrigerator it is stable for 2 to 3 months. When 5 ml of this reagent are added to 100 ml of distilled water containing no fluorides, it soon turns pink. Fluorides discharge the pink colour of the lake so that the solution acquires a more yellow tint.

23.2.4 *Silver Sulphate*

23.2.5 *Perchloric Acid* — 60 percent.

23.2.6 *Phenolphthalein Indicator* — same as in **14.1.1.**

23.2.7 *Sodium Hydroxide Solution* — 10 percent *w/v.*

23.2.8 *Concentrated Sulphuric Acid* — conforming to IS : 266-1961†.

23.3 Procedure — Two methods are prescribed below. The method without distillation (described under **23.3.1**) is reliable for samples in which the interfering substances are not in excess of the limits given below:

a) Chlorides (as Cl)	2 000 mg/l
b) Sulphates (as SO_4)	300 mg/l
c) Alkalinity (as $CaCO_3$)	400 mg/l
d) Iron (as Fe)	2 mg/l
e) Aluminium (as Al)	0·5 mg/l
f) Phosphates (as PO_4)	5 mg/l

*Specification for hydrochloric acid (*revised*).
†Specification for sulphuric acid (*revised*).

Where the sample is highly coloured or turbid or has interfering substances in excess of the limits given above, the method with distillation (described under **23.3.2**) shall be used or the sample shall be appropriately diluted before this test. With samples of unknown composition or where greater accuracy is needed, the method with distillation shall be employed.

23.3.1 *Method Without Distillation*

23.3.1.1 The sample shall not contain free chlorine; if necessary, it shall be dechlorinated with a slight excess of sodium thiosulphate solution before use.

23.3.1.2 Take 100 ml of the clear sample and a series of dilutions of standard sodium fluoride solution in 100 ml of distilled water in Nessler tubes and add 5·0 ml of the zirconium alizarin reagent to each. The sample and standards shall be at the same temperature to within 1° to 2°C. Mix and compare the colours after standing for one hour exactly. Note the volume of standard sodium fluoride solution contained in the tube with which a match with the sample under test is obtained. If the fluoride content is over 1·0 mg/l, the determination shall be repeated after suitable dilution.

23.3.2 *Method with Distillation*

23.3.2.1 Introduce into the Claisen flask a number of fragments of Pyrex glass or glass beads, 0·2 g of silver sulphate, 7 ml of distilled water and 15 ml of perchloric acid. Heat the flask until the temperature reaches 120° to 125°C, connect to the steam supply and regulate the gas and steam so that the distillation proceeds at a temperature of 137° to 140°C. Distil 150 ml in 25 to 35 minutes and steam out the condenser towards the end of the distillation. Discard the first distillate. Distil a further 150 ml and determine the fluorides in it by the method given in **23.3.1.2**. The figure for this blank shall not exceed 0·001 5 mg and shall be approximately constant for any further 150-ml fraction.

23.3.2.2 Make 150 ml of the sample alkaline to phenolphthalein indicator with sodium hydroxide solution, add a few drops in excess and concentrate to 20 ml. When cool, transfer quantitatively to the distillation flask and carefully add 15 ml of concentrated sulphuric acid. If the amount of chloride in the aliquot exceeds 5 mg, add about 5 mg of silver sulphate for each milligram of chlorine. Connect up the apparatus and distil 150 ml as in **23.3.2.1**. Determine the fluoride content of the total 150 ml of distillate as in **23.3.1.2**.

23.4 Calculation

23.4.1 *Method Without Distillation*

$$\text{Fluorides (as F), mg/l} = \frac{1\,000\ W}{V}$$

where

W = weight in mg of fluorides (as F) in the standard solution matched by the sample, and

V = volume in ml of the sample taken for the test.

23.4.2 *Method with Distillation*

$$\text{Fluorides (as F), mg/l} = \frac{1\,000\ W}{V}$$

where

W = weight in mg of fluorides (as F) in the standard solution matched by 150 ml of the distillate, and

V = volume in ml of the sample taken for the test in **23.3.2.2.**

23.5 Precision and Accuracy — The recovery by distillation is quantitative. The precision and accuracy of the colorimetric method depend upon time and temperature control and the effect of interfering substances. When the procedure is carefully followed and interference is low, the precision and accuracy are both $\pm 0{\cdot}1$ mg/l.

24. CHLORIDES

24.0 Outline of the Method — The sample after neutralization is titrated against standard silver nitrate solution using potassium chromate indicator.

24.1 Reagents

24.1.1 *Aluminium Hydroxide Suspension* — Dissolve 125 g of potassium or ammonium alum in 1 litre of distilled water. Precipitate the aluminium by adding ammonium hydroxide slowly and with stirring. Wash the precipitate by successive decantation with several portions of distilled water until free from sulphates.

24.1.2 *Hydrogen Peroxide* — 30 percent.

24.1.3 *Calcium Carbonate*

24.1.4 *Standard Nitric Acid* — 0·1 N.

24.1.5 *Potassium Chromate Solution* — Dissolve 5 g of potassium chromate in distilled water and make up to 100 ml. Add silver nitrate solution to produce a slight red precipitate and filter.

24.1.6 *Standard Silver Nitrate Solution* — Dissolve 4·791 g of silver nitrate, dried at 105° ± 2°C, in distilled water and make up to 1 000 ml. One millilitre of the solution is equivalent to 1 mg of chlorides (as Cl). Standardize with a standard chloride solution. The solution shall be kept in the dark.

24.2 Procedure

24.2.1 Use 100 ml of the sample, filtered if necessary, for the titration. If the sample is coloured, decolorize by adding 3 ml of aluminium hydroxide suspension. Stir thoroughly and after a few minutes filter and wash with 10 to 15 ml of distilled water. If sulphites are present, add 1 ml of hydrogen peroxide with stirring.

24.2.2 Place the sample treated as in **24.2.1** in a porcelain basin. If the *p*H of the sample is less than 6·8, add a small amount of calcium carbonate to the sample in the basin so as to neutralize the acidity. If the *p*H is above 10, determine the amount of standard nitric acid required to neutralize 100 ml of the sample, and add this amount of the acid to the portion used for the chloride determination, and then add a trace of calcium carbonate. Add 1 ml of potassium chromate solution and titrate with standard silver nitrate solution with constant stirring until there is perceptible reddish colouration. Subtract 0·2 ml from the titration figure to allow for the excess of reagent required to form silver chromate.

NOTE — If the sample requires more than 25 ml of silver nitrate solution, repeat the determination with a smaller quantity of the sample diluted to 100 ml with distilled water. If chlorides are present in very small quantities, concentrate 500 or 1 000 ml in a porcelain dish to 100 ml, rub down sides of the dish carefully, neutralize as above and titrate with silver nitrate solution.

24.3 Calculation

$$\text{Chlorides (as Cl), mg/l} = \frac{1\,000 \times V_1 \times f}{V_2}$$

where

V_1 = volume in ml of standard silver nitrate solution used in the titration,

f = mg of chloride (as Cl) equivalent to 1 ml of silver nitrate solution, and

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

24.4 Precision and Accuracy — The precision and accuracy are limited by the accuracy of detection of the end point which is usually about 0·2 ml, or 0·1 mg of chloride, and by the presence of interfering substances.

25. IODIDES

25.0 General — Two methods are prescribed. The colorimetric method described in **25.1** is only approximately accurate and may be used as an alternate method. The volumetric method described in **25.2** shall be the referee method.

25.1 Colorimetric Method

25.1.0 *Outline of the Method* — The iodides in the sample are oxidized with nitrous acid. The liberated iodine after extraction in carbon disulphide, is matched against a series of standard iodine solutions.

25.1.1 *Apparatus*

25.1.1.1 *Nessler tubes* — 50 ml capacity.

25.1.2 *Reagents*

25.1.2.1 *Sodium carbonate*

25.1.2.2 *Rectified spirit* — conforming to IS : 323-1959*.

25.1.2.3 *Sodium hydroxide solution* — 10 percent *w/v*.

25.1.2.4 *Dilute sulphuric acid* — 1 : 5 *v/v*.

25.1.2.5 *Sodium nitrite solution* — 0·2 percent *w/v*.

25.1.2.6 *Carbon disulphide*

25.1.2.7 *Standard potassium iodide solution* — Dissolve 0·328 g of potassium iodide in distilled water and make up to 250 ml. Dilute 50 ml to 250 ml; one millilitre of the diluted solution contains 0·2 mg of iodides (as I).

25.1.3 *Procedure* — Evaporate 0·5 to 2 litres of the sample to dryness after addition of small quantity of sodium carbonate. Boil the residue thus obtained with distilled water, transfer to filter and wash thoroughly with hot distilled water. Dilute the alkaline filtrate to a definite volume. Evaporate to dryness an aliquot of the alkaline filtrate, add 2 to 3 ml of distilled water to dissolve the residue and enough rectified spirit to make percentage by volume of alcohol about 90 (this precipitates the chlorides). Heat to boiling, filter, and repeat the preceding operation of solution and precipitation once or twice. Add 2 to 3 drops of sodium hydroxide solution to the combined alcoholic filtrates and evaporate to dryness. Dissolve this last residue in 2 to 3 ml of distilled water and repeat precipitation with rectified spirit, heating and filtering. Add a drop of sodium hydroxide solution to this alcoholic filtrate and evaporate to dryness. Dissolve this residue in a little distilled water, acidify with dilute sulphuric acid, using 3 or 4 drops in excess and transfer to a small flask. Add 4 drops of sodium nitrite solution and about 5 ml of carbon disulphide. Shake until all the iodine is extracted and filter off the acid solution from the carbon disulphide. Wash the flask, filter and wash contents with cold distilled water. Repeat once again the extraction of aqueous filtrate and washings with 5 ml of carbon disulphide. Transfer both the carbon disulphide extracts to a Nessler tube and make the contents of the Nessler tube to a definite volume, usually 12 to 15 ml. Compare the colour of the carbon disulphide layer with that obtained with different quantities of iodine dissolved in carbon disulphide under similar conditions. Exact quantities of iodine may be produced by taking measured

*Specification for rectified spirit (*revised*).

conditions. Exact quantities of iodine may be produced by taking measured quantities of standard potassium iodide solution and treating as above. Preserve the aqueous solutions from the sample and the standards for determination of bromide in **26.3.**

NOTE — Results closely approximating the true values for iodides may be obtained in a shorter time on most samples by omitting the extractions with rectified spirit.

25.1.4 *Calculation*

$$\text{Iodides (as I), mg/l} = \frac{1\,000\ Wf}{V}$$

where

W = mg of iodine present in the matching control standard,

f = factor representing the aliquot of the alkaline filtrate tested, and

V = volume in ml of the sample taken for the test.

25.2 Volumetric Method

25.2.0 *Outline of the Method* — The iodides are oxidized with bromine water to iodine which is then titrated against standard thiosulphate solution.

25.2.1 *Reagents*

25.2.1.1 *Sodium carbonate*

25.2.1.2 *Methyl orange indicator solution* — same as in **13.1.2.**

25.2.1.3 *Standard sulphuric acid* — 2 N.

25.2.1.4 *Bromine water*

25.2.1.5 *Sodium sulphite solution* — 1 percent *w/v.*

25.2.1.6 *Phenol solution* — 5 percent *w/v.*

25.2.1.7 *Potassium iodide solution* — 10 percent *w/v.*

25.2.1.8 *Standard sodium thiosulphate solution* — 0·005 N

25.2.1.9 *Starch indicator solution* — Triturate 5 g of starch and 0·01 g of mercuric iodide with 30 ml of cold distilled water and slowly pour it with constant stirring into 1 litre of boiling distilled water. Boil for 3 minutes. Allow to cool and decant off the supernatant clear liquid.

25.2.2 *Procedure* — Neutralize an aliquot of the alkaline filtrate obtained as in **25.1.3** to methyl orange with standard sulphuric acid. Add bromine water dropwise from a burette in an amount equivalent to 20 mg of bromine. After a few minutes, destroy greater portion of remaining free bromine by adding sodium sulphite solution dropwise while mixing. Wash down neck and sides of the flask with distilled water and complete the removal of free bromine by addition of 1 to 2 drops of phenol solution. Add 1 ml of standard sulphuric acid and 5 ml of potassium iodide solution and titrate liberated iodine with standard sodium thiosulphate solution, adding 1 ml of starch

indicator near the end of the titration. Correct the determination for blank on reagents.

25.2.3 *Calculation*

$$\text{Iodides (as I), mg/l} = \frac{634{\cdot}6\ V_1 f}{V}$$

where

V_1 = volume in ml of standard sodium thiosulphate solution used in the titration,

f = factor representing the aliquot of the alkaline filtrate taken for titration, and

V_2 = volume in ml of the sample taken for the test in **25.1.3.**

26. BROMIDES

26.0 Outline of the Method — Bromides in the sample are oxidized to bromine which is then extracted with carbon disulphide, and the colour obtained is matched with that produced with a series of standard bromine solutions.

26.1 Apparatus

26.1.1 *Nessler Tubes* — 50 ml capacity.

26.2 Reagents

26.2.1 *Standard Potassium Bromide Solution* — Dissolve 0·372 g of potassium bromide in distilled water and make up to 250 ml. Dilute 50 ml to 250 ml. One millilitre of the diluted solution contains 0·2 mg of bromides (as Br).

26.2.2 *Chlorine Water* — saturated and freshly prepared.

26.2.3 *Carbon disulphide*

26.3 Procedure — Transfer separately to small flasks the aqueous solutions of the sample and the standards preserved in **25.1.3.** To the standards, add definite measured quantities of standard potassium bromide solution and to each of the flasks containing the sample and the standards, add 5 ml of carbon disulphide. Add chlorine water, 1 ml at a time shaking after each addition until all the bromine is set free. Avoid a large excess of chlorine as a bromochloride may form and spoil the colour reaction. Filter off the aqueous solution from the carbon disulphide through moistened filter, wash the contents of the filter 2 or 3 times with distilled water, and transfer the carbon disulphide solution to a Nessler tube by means of about 1 ml of carbon disulphide. Repeat this extraction of filtrate and aqueous washings twice, using 3 ml of carbon disulphide each time. Combined carbon disulphide

extracts usually amount to 11·5 to 12 ml. Add enough carbon disulphide to bring the contents to a definite volume, usually 12 to 15 ml and compare the colour obtained with that produced by standards.

NOTE — If quantities of carbon disulphide recommended do not extract all the bromine, make one or two extra extractions with carbon disulphide, transfer extracts to another Nessler tube and compare the colour with some lower standards. Add readings thus obtained to the others.

26.4 Calculation

$$\text{Bromides (as Br), mg/l} = \frac{1\,000\ Wf}{V}$$

where

W = mg of bromine present in the matching control standard,

f = factor representing the aliquot of the alkaline filtrate tested in **25.1.3**, and

V = volume in ml of the sample taken for the test in **25.1.3**.

27. CYANIDES

27.0 Outline of the Method — The cyanides are removed by distillation and reacted with chloramine-T and pyridine-pyrazolone reagent. The colour developed is matched against that produced with a series of standard cyanide solutions.

27.1 Reagents

27.1.1 *Tartaric Acid Solution* — 15 percent *w/v*.

27.1.2 *Sodium Hydroxide Solution* — 2 percent *w/v*.

27.1.3 *Dilute Acetic Acid* — 1 : 4 *v/v*.

27.1.4 *Chloramine-T Solution* — Prepare a one percent aqueous solution, fresh daily.

27.1.5 *Mixed Pyridine-Pyrazolone Reagent*

a) Prepare a saturated aqueous solution of 1-phenyl-3-methyl-5-pyrazolone (solubility approximately 0·5 g/100 ml) by adding the pyrazolone to distilled water at approximately 75°C. Agitate occasionally as the solution cools to room temperature.

b) Dissolve 17·4 g of 1-phenyl-3-methyl-5-pyrazolone in 100 ml of rectified spirit (conforming to IS : 323-1959*) and add 25 g of phenyl hydrazine, freshly distilled under reduced pressure. Reflux in an all-glass apparatus. Several hours of refluxing are necessary

*Specification for rectified spirit (*revised*).

to produce bis-pyrazolone which is indicated by formation of crystals in the reflux mixture. A reflux of 6 to 8 hours followed by standing at room temperature overnight and 1 to 2 hours reflux the following day is generally adequate for a good yield. Filter while hot, wash with hot rectified spirit and dry in air. The product, melting point greater than 320°C, is stable indefinitely in dry form.

c) Mix 125 ml of the filtered saturated aqueous solution of the pyrazolone prepared in (a) above with a filtered solution containing 0·025 g of bis-pyrazolone, prepared in (b) above, dissolved in 25 ml of pyridine. Several minutes of mixing are usually necessary to dissolve the bis-pyrazolone in pyridine. The mixed reagent develops a pink colour on standing but this does not affect the colour development with cyanide if used within 24 hours.

27.1.6 *Stock Cyanide Solution* — Dissolve 2·51 g of potassium cyanide in 1 litre of distilled water. Standardize with silver nitrate solution. The solution loses strength gradually and shall be re-checked every week.

27.1.7 *Standard Cyanide Solution* — Dilute 10 ml or an appropriate volume of stock cyanide solution to 1 litre with distilled water, mix and make a second dilution of 10 ml to 100 ml. One millilitre of the diluted solution shall contain 1 μg of cyanide (as CN). This solution shall be freshly prepared at frequent intervals.

27.1.8 *Disodium Phosphate Solution* — Dissolve 5 g of anhydrous disodium hydrogen phosphate in 100 ml of distilled water.

27.1.9 *n-Butyl Alcohol*

27.2 Procedure

27.2.1 Titrate a portion of the sample with tartaric acid solution to approximately *p*H 5·0. Record the volume of sample and acid required, then discard the aliquot used. Add the volume of sample to be used for test to a distillation flask. If necessary dilute the sample to 300 ml with distilled water. Use pumice stone or glass beads to prevent bumping. Place 50 ml of sodium hydroxide solution in a 500-ml receiving cylinder and adjust the delivery tube from the condenser so that it releases the distillate within 5 mm of the bottom of the receiving cylinder or well below the surface of the sodium hydroxide solution. Adjust the condenser cooling water. On the basis of the preliminary titration with tartaric acid solution, calculate the volume of acid necessary to reduce the *p*H of the solution in the flask to approximately *p*H 5·0. Add this volume of acid to the sample and add 5·0 ml more. Stopper the flask immediately and make sure that the joint between the condenser and the flask is tight. Heat the contents of the flask to boiling and carefully distil over exactly 250 ml. The distillate and

the sodium hydroxide solution in the receiving cylinder shall then be mixed. The mixed liquid is referred to as *absorption liquid* in the subsequent text.

27.2.2 An aliquot of the *absorption liquid* shall be neutralized with dilute acetic acid to *p*H 6 to 7. A correction factor shall be used in the calculation of results if the volume change is significant.

27.2.3 Place a series of dilutions of the neutralized aliquot containing the desired cyanide concentrations in a set of reaction tubes which, together with their stoppers, have been carefully rinsed with distilled water. Include a blank containing all reagents but no cyanide and a control standard containing a known amount of standard cyanide solution. Distilled water shall be added, if necessary, to a volume of approximately 15 ml. Add 0·2 ml of chloramine-T solution, stopper and mix by inversion two or three times. Allow 1 to 2 minutes for the reaction. Add 5·0 ml of the mixed pyridine-pyrazolone reagent, stopper and mix by inversion. Allow 20 minutes for colour development.

27.2.4 If the colour is to be measured in aqueous phase, dilute all reaction tubes accurately to a definite volume, usually 25 ml, mix and read absorbance at 620 mμ of sample aliquots and control standard. Note the dilution in the tube the colour of which is a nearest match to that of the control tube. If colour is too intense, repeat the test using a smaller sample or aliquot.

27.2.5 Greater sensitivity is possible if the extracted colour is used for spectrophotometric reading. At the end of the colour development period, add 1 ml of disodium phosphate solution and exactly 10 ml of *n*-butyl alcohol. Stopper and mix by inversion. If the emulsion formed does not break within 1 to 3 minutes, add more of the phosphate solution and mix again. Withdraw an aliquot of the butyl alcohol layer and measure the absorbance at 630 mμ. A large sample volume or trace quantities of cyanide may require a modified solvent volume.

NOTE — The pyridine pyrazolone colour will not develop in a quantitative manner in the butyl alcohol layer or if the phosphate is added before the colour development is essentially complete in the aqueous phase.

27.3 Calculation

$$\text{Cyanides (as CN), mg/l} = \frac{A_1}{A_2 V} \times B \times C \times D$$

where

A_1 = absorbance of the aliquot of the neutralized *absorption liquid* which gives the nearest match with that of the control standard,

A_2 = absorbance of the control standard,

V = volume in ml of the neutralized *absorption liquid* taken in the tube which gives the nearest match with the control standard,

B = µg of cyanides in the control standard,

C = dilution factor in distillation, that is, total volume in ml of *absorption liquid* prepared after distillation in **27.2.1** divided by the volume in ml of the original sample taken for distillation, and

D = dilution factor for colour development, that is, total volume in ml of the neutralized *absorption liquid* prepared for colour test in **27.2.2** divided by the volume in ml of the neutralized *absorption liquid* taken in the reaction tube which gives a match with the control standard in **27.2.4** or **27.2.5**.

28. SELENIUM

28.0 Outline of the Method — Selenium is removed by distillation as selenium bromide. The selenious acid obtained is reduced with hydroxylamine hydrochloride to elemental selenium in the form of a very pale pink colloidal suspension which is matched against a series of standard selenium solutions.

28.1 Apparatus

28.1.1 *Nessler Tubes* — 100 ml capacity.

28.2 Reagents

28.2.1 *Sodium Peroxide*

28.2.2 *Sulphuric-Nitric Acid Mixture* — Cautiously add 1 part of concentrated sulphuric acid (conforming to IS : 266-1961*) to 2 parts of concentrated nitric acid (conforming to IS : 264-1950†).

28.2.3 *Hydrobromic Acid* — 48 percent. Reserve for this determination a supply of hydrobromic acid which becomes completely decolourized when subjected to the sulphur dioxide treatment as described in **28.3.3**. If the reagent in stock does not meet this requirement, purify it by distillation in an all-glass still, collecting the middle fraction of the distillate.

28.2.4 *Hydrobromic Acid-Bromine Reagent* — Mix 15 ml of bromine with 985 ml of hydrobromic acid.

28.2.5 *Concentrated Sulphuric Acid* — conforming to IS : 266-1961*.

*Specification for sulphuric acid (*revised*).

†Specification for nitric acid.

28.2.6 *Sulphur Dioxide Gas*

28.2.7 *Gum Arabic Solution* — 5 percent, aqueous. This solution is subject to bacterial growths and shall either be prepared as needed or preserved by saturating it with benzoic acid.

28.2.8 *Hydroxylamine Hydrochloride Solution* — 10 percent *w/v*.

28.2.9 *Selenium Stock Solution* — Selenium dioxide of known high degree of purity, dried to constant weight in an oven at 150°C and cooled over phosphorus pentoxide in a desiccator, shall be used for preparing this solution. Dissolve in distilled water the equivalent of 1·405 g of selenium dioxide, add about 80 ml of hydrobromic acid and dilute with distilled water to 1 litre.

28.2.10 *Standard Selenium Solution* — Place 100 ml of the stock solution in a 1-litre volumetric flask, add 10 ml of hydrobromic acid and dilute to the mark with distilled water. It is best not to allow the acidity, determined by titration, to fall below 0·05 N since neutral or very slightly acid solutions of dilute selenious acid tend to lose their titre. One millilitre of this solution is equivalent to 0·1 mg of selenium (as Se).

28.3 Procedure

28.3.1 Use 1 to 10 litres of the sample containing not more than 0·5 mg of selenium (as Se) and add sufficient amount of fresh sodium peroxide to make the liquid just alkaline. Evaporate nearly to dryness on a steam-bath. Evaporation may be hastened by using an electric hot-plate if care is taken not to allow the sample to become dry. In any case, evaporation of the last 100 ml shall be done on the steam-bath. If a high concentration of sewage or other organic matter is present, it may be necessary to digest the residue with a few drops of sulphuric-nitric acid mixture to oxidize the organic matter before the distillation is carried out.

28.3.2 Transfer the residue with washings to a distillation flask and add 50 ml of hydrobromic acid and 5 to 10 ml of hydrobromic acid-bromine reagent and, while cooling under running water and swirling, slowly and carefully add a volume of concentrated sulphuric acid approximately equal to that of the water present with the transferred residue. Before starting the distillation, arrange the receiver so that a minimum amount of hydrobromic acid-bromine solution will be needed to just cover the tip of the adapter, otherwise some of the selenium bromide may escape into the air. Distil gradually until all the selenium bromide and most of the hydrobromic acid have passed over. The distillation should take about 30 minutes and the volume of the distillate should be about 75 to 90 ml.

(*Caution* — The distillation shall be conducted in an efficient fume hood because of the copious evolution of bromine fumes.)

28.3.3 Transfer the distillate to an appropriate sized beaker and pass in sulphur dioxide gas until the yellow colour due to bromine is discharged. Continue treating with sulphur dioxide for 5 seconds more. Add 1 ml of gum arabic solution and 2 ml of hydroxylamine hydrochloride solution and mix. Cover with a watch-glass and allow to stand for 1 hour. Make up to 100 ml, mix well, and transfer to a Nessler tube. Compare visually with standards as prepared in **28.3.4**.

28.3.4 A known quantity of standard selenium solution shall be evaporated nearly to dryness and transferred with washings to the distillation flask and treated as described above. Make up to 100 ml and mix thoroughly. Make the desired standards by diluting appropriate amounts of this solution to the mark in Nessler tubes. Visual comparison shall be used because the colour system is very pale pink and is best carried out in sunlight. It is difficult to match solutions containing more than 0·5 mg of selenium in 50 ml; the colour comparison is most satisfactory when 0·01 to 0·10 mg of selenium (as Se) is present.

28.4 Calculation

$$\text{Selenium (as Se), mg/l} = \frac{1\,000\,A}{V}$$

where

A = amount in mg of selenium present in the control standard which matches exactly the colour obtained with the sample, and

V = volume in ml of the sample taken for the test.

28.5 Precision and Accuracy — This method is said to give low results but when considering concentrations of the magnitude of 0·005 to 0·10 mg/l, the relative error may not be significant.

29. BORON

29.0 General

29.0.1 Two methods are prescribed. Method A is applicable in the range 0·000 2 to 0·008 mg of boron (as B) and Method B is applicable in the range 0·001 to 0·05 mg of boron (as B). Fluorides, nitrates, ferricyanides and other oxidizing agents interfere.

29.0.2 *Outline of the Method* — Boron in the sample is treated with an excess of sulphuric acid and quinalizarin solution. The colour obtained is matched against that produced with a series of standard boron solutions.

29.1 Method A

29.1.1 *Apparatus*

29.1.1.1 *Nessler tubes* — matched.

29.1.2 *Reagents*

29.1.2.1 *Concentrated sulphuric acid* — not less than 98 percent *w/w* and nitrate-free.

29.1.2.2 *Dilute sulphuric acid* — prepared by diluting 9 volumes of concentrated sulphuric acid with 1 volume of distilled water.

29.1.2.3 *Quinalizarin solution* — Dissolve 0·01 g in 100 ml of dilute sulphuric acid.

29.1.2.4 *Standard boron solution* — Dissolve 0·057 g of boric acid in 100 ml of dilute sulphuric acid. Dilute 1·0 ml of the solution again to 100 ml with dilute sulphuric acid. One millilitre of the diluted solution is equivalent to 0·001 mg of boron (as B).

29.1.3 *Procedure* — Transfer by means of a pipette 1·0 ml of the sample to a Nessler tube, add from a burette 9 ml of concentrated sulphuric acid, mix and cool the solution. In another Nessler tube, place 10 ml of dilute sulphuric acid and add 0·5 ml of quinalizarin solution to each tube. Mix the solutions well. Prepare for colour comparison a series of standards by taking different volumes of standard boron solution and diluting to 10 ml with dilute sulphuric acid. Add 0·5 ml of quinalizarin solution to each tube, mix and allow to stand for 5 minutes. Match the colour obtained with the sample with that obtained with the standards.

29.1.4 *Calculation*

$$\text{Boron (as B), mg/l} = V$$

where

V = volume in ml of standard boron solution required to match the colour obtained with the sample.

29.1.5 *Accuracy* — The accuracy of the method is 0·000 2 mg of boron (as B).

29.2 Method B

29.2.1 *Apparatus*

29.2.1.1 *Nessler tubes* — same as in **29.1.1.1**.

29.2.2 *Reagents*

29.2.2.1 *Concentrated sulphuric acid* — same as in **29.1.2.1**.

29.2.2.2 *Dilute sulphuric acid* — prepared by diluting 4 volumes of concentrated sulphuric acid with 1 volume of distilled water.

29.2.2.3 *Quinalizarin solution* — Dissolve 0·01 g in 100 ml of dilute sulphuric acid.

29.2.2.4 *Standard boron solution* — Dissolve 0·286 g of boric acid in 100 ml of dilute sulphuric acid. Dilute 1·0 ml of the solution again to 100 ml with dilute sulphuric acid. One millilitre of the diluted solution is equivalent to 0·005 mg of boron (as B).

29.2.3 *Procedure* — Transfer by means of a pipette 2·0 ml of the sample and carry out the determination exactly as described in **29.1.3.**

29.2.4 *Calculation*

$$\text{Boron (as B), mg/l} = 2{\cdot}5\ V$$

where

V = volume in ml of standard boron solution required to match the colour obtained with the sample.

29.2.5 *Accuracy* — The accuracy of the method is 0·001 mg of boron (as B)

30. SILICA

30.0 General — Two methods are prescribed for the determination of silica. The gravimetric method given in **30.1** is applicable to any sample of industrial water and shall be the referee method. The colorimetric method given in **30.2** may be used only for samples that are neither coloured nor turbid.

30.1 Gravimetric Method

30.1.0 *Outline of the Method* — Silica is precipitated by evaporation with hydrochloric acid and nitric acid. The precipitate obtained is treated with sulphuric acid and hydrofluoric acid. The loss in weight on heating with hydrofluoric acid gives silica content.

30.1.1 *Reagents* — It is recommended that all reagents given below are stored in polyethylene bottles.

30.1.1.1 *Methyl orange indicator* — same as in **13.1.2.**

30.1.1.2 *Concentrated hydrochloric acid* — conforming to IS : 265-1962*.

30.1.1.3 *Concentrated nitric acid* — conforming to IS : 264-1950†.

30.1.1.4 *Perchloric acid* — 70 percent *w/w.*

30.1.1.5 *Dilute hydrochloric acid* — Dilute 2 volumes of concentrated hydrochloric acid with 98 volumes of distilled water.

30.1.1.6 *Concentrated sulphuric acid* — conforming to IS : 266-1961‡.

*Specification for hydrochloric acid (*revised*).

†Specification for nitric acid.

‡Specification for sulphuric acid (*revised*).

30.1.1.7 *Hydrofluoric acid* — 48 to 51 percent *w/w*.

30.1.2 *Procedure*

30.1.2.1 Test the sample with methyl orange indicator. If the sample is alkaline to methyl orange, add to a volume of the sample containing not less than 5 mg of silica (as SiO_2) sufficient concentrated hydrochloric acid to neutralize it and provide a 5-ml excess of the acid. If the sample is originally acid to methyl orange, add only 5 ml of concentrated hydrochloric acid without any neutralization. Evaporate the acidified sample to approximately 100 ml in a 400-ml, scratch-free, low-form, chemically resistant glass beaker (*see* Note) on a water-bath or hot-plate, under a fume hood. Add 30 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid and continue evaporation to a volume of approximately 20 ml. Add 20 ml of concentrated nitric acid and 10 ml of perchloric acid and again evaporate on a hot-plate under a fume hood until dense white fumes of perchloric acid appear and the concentrated liquid is boiling. Continue to boil the concentrate for 10 minutes.

NOTE — If the silica content is so low that a very large quantity of the sample has to be evaporated, do not increase the size of the beaker but periodically replenish the evaporating liquid with increments from the acidified sample reservoir.

30.1.2.2 Cool the concentrate and add 50 ml of distilled water. Boil the diluted solution for several minutes and filter it through an ashless medium texture filter paper. Wash the residue on the filter paper with at least 15 portions of hot dilute hydrochloric acid to remove the perchloric acid. It is important to wash the entire filter paper, including the extreme upper edge, to prevent sparking during ignition of the residue. Place the filter paper with the residue in a weighed platinum crucible, dry and char the paper without flaming it and then ignite the charred residue for 30 minutes at 1 000° to 1 200°C to constant weight (W_1).

30.1.2.3 To the weighed residue, add several drops of concentrated sulphuric acid and 5 ml of hydrofluoric acid and evaporate to dryness on a low-temperature hot-plate or water-bath under a fume hood. Re-ignite the residue at 1 000° to 1 200°C to constant weight (W_2).

30.1.2.4 Carry out a blank by making an identical determination on the quantity of distilled water required for washing and diluting in **30.1.2.2**.

30.1.3 *Calculation*

$$\text{Silica (as } SiO_2\text{), mg/l} = \frac{(W_1 - W_2) - (W_3 - W_4)}{V}$$

where

W_1 = weight in mg of the residue obtained in **30.1.2.2**,

W_2 = weight in mg of the residue obtained in **30.1.2.3**,

W_3 = weight in mg of the residue before treatment with hydrofluoric acid in **30.1.2.4**,

W_4 = weight in mg of the residue after treatment with hydrofluoric acid in **30.1.2.4**, and

V = volume in litres of the sample taken for the test.

30.1.4 *Precision and Accuracy* — The precision and accuracy are essentially equal and are limited by balance reproducibility and the volume of the sample used. If the balance is reproducible to 0·1 mg, the maximum variation in precision is of the order of 0·4 mg.

30.2 Colorimetric Method

30.2.0 *Outline of the Method* — The silicomolybdic acid is reduced by hydroquinone and the yellow colour obtained is matched against that produced with a series of standard silica solutions.

30.2.1 *Apparatus*

30.2.1.1 *Nessler tubes* — 50 ml capacity.

30.2.2 *Reagents* — It is recommended that all reagents are stored in polyethylene bottles.

30.2.2.1 *Ammonium molybdate solution* — 10 percent *w/v*.

30.2.2.2 *Dilute sulphuric acid* — approximately 2 N.

30.2.2.3 *Sodium citrate solution* — 30 percent *w/v* solution of trisodium citrate dihydrate.

30.2.2.4 *Hydroquinone solution* — Add 1 ml of sulphuric acid (1 N) to 5 g of hydroquinone, dilute to 100 ml with distilled water and shake to dissolve.

30.2.2.5 *Sodium sulphite solution* — Dissolve, just before use, 20 g of sodium sulphite heptahydrate in water and dilute to 100 ml.

30.2.2.6 *Standard silica solution* — Fuse 0·500 g of powdered silica with 5 g of sodium carbonate in a platinum crucible until all the silica is dissolved in the molten sodium carbonate. Cool and extract the melt with hot water. When all the solid is dissolved, add 2 to 3 g of sodium hydroxide, make up to 500 ml and store in a polyethylene bottle. One millilitre of this solution contains one milligram of silica (as SiO_2). Just before use, dilute this solution appropriately so that one millilitre of the diluted solution contains, for **30.2.3.2**, 0·005 mg; and for **30.2.3.3**, 0·025 mg; of silica (as SiO_2).

30.2.3 *Procedure*

30.2.3.1 Measure 25 ml of the sample into a Nessler tube and place it in a water-bath at a temperature of 25° ± 1°C. When the sample has reached the temperature of the bath, add 1·0 ml of ammonium molybdate solution and 2·0 ml of dilute sulphuric acid. Mix, allow to stand in the

water-bath for 10 minutes, add 2·0 ml of sodium citrate solution and mix again. Add 2·0 ml of hydroquinone solution and mix. Add 3·0 ml of sodium sulphite solution, dilute to 50 ml and shake well. Allow to stand for 15 minutes at a temperature of 25° ± 1°C. Prepare a blank using distilled water and complete the determination by one of the following methods given in **30.2.3.2** or **30.2.3.3**, allowing for the blank.

30.2.3.2 *For silica content up to 0·025 mg* — Into eight Nessler tubes, measure by means of a burette 0·0, 0·5, 1·0, 1·5, 2·0, 3·0, 4·0 and 5·0 ml of standard silica solution (1 ml ≡ 0·005 mg SiO_2) and dilute to 25 ml. Treat in the same manner as the sample and compare the colour obtained with the sample and the standards against a white background.

30.2.3.3 *For silica content above 0·025 mg* — Into nine Nessler tubes, measure by means of a burette 1·0, 1·5, 2·0, 2·5, 3·0, 3·5, 4·0, 4·5 and 5·0 ml of standard silica solution (1 ml ≡ 0·025 mg SiO_2) and dilute to 25 ml. Treat in the same manner as the sample and compare the colour obtained with the sample and the standards against a white background.

30.2.4 *Calculation*

$$\text{Silica (as } SiO_2\text{), mg/l} = 40W$$

where

W = weight in mg of silica in the Nessler tube matching the colour obtained with the sample.

30.2.5 *Range* — This colorimetric method is applicable up to a range of 0·125 mg of silica (as SiO_2). If the phosphate content (as PO_4) is less than 50 mg/l it will not interfere with the determination.

31. ALUMINIUM

31.0 Outline of the Method — After removal of iron, the sample is treated with glycerine and hematoxylin; the colour developed is matched against that produced with a series of standard aluminium solutions.

31.1 Apparatus

31.1.1 *Nessler Tubes* — 50 ml capacity.

31.2 Reagents

31.2.1 *Standard Aluminium Solution* — Dissolve 1·759 g of aluminium potassium sulphate [$K_2SO_4.Al_2(SO_4)_3.24H_2O$] in distilled water containing 50 ml of exactly 5 N hydrochloric acid and dilute to 1 litre. One millilitre of this solution contains 0·1 mg of aluminium (as Al). Before use, dilute this stock solution appropriately so that one millilitre of the diluted solution is equivalent to 0·01 mg and 0·002 mg of aluminium (as Al).

31.2.2 *Dilute Hydrochloric Acid* — exactly 5 N.

31.2.3 *Bromine Water* — saturated solution.

31.2.4 *Ammonium Thiocyanate Solution* — 8 percent *w/v*.

31.2.5 *Extraction Solvent* — Mix 5 volumes of amyl alcohol with 2 volumes of solvent ether.

31.2.6 *A onium Carbonate Solution* — exactly 2 N, standardized against standard hydrochloric acid.

31.2.7 *Glycerine Solution* — Dilute one volume of glycerine with one volume of distilled water.

31.2.8 *Hematoxylin Solution* — Weigh 0·1 g of hematoxylin and dissolve in 100 ml of cold distilled water containing 0·1 ml of dilute hydrochloric acid.

31.2.9 *Ammonium Borate Solution* — 0·8 N. Dissolve 93 g of powdered boric acid in 1 litre of ammonium hydroxide (1 N). Filter and dilute with distilled water to the desired strength, standardizing against standard hydrochloric acid.

31.3 Procedure

31.3.1 Immediately after shaking the sample, measure accurately into a 100-ml conical flask a volume of the sample that will contain from 0·001 to 0·005 mg of aluminium. Measure a blank of distilled water of the same volume as the sample into a 100-ml conical flask. Prepare a set of solutions for comparison by measuring out into a series of 100-ml conical flasks progressively increasing volumes of standard aluminium solution (1 ml $\equiv$ 0·01 mg or 1 ml $\equiv$ 0·002 mg, as necessary) and diluting each to the volume of the sample with distilled water.

31.3.2 To each of the series of conical flasks, add 1·0 ml of dilute hydrochloric acid. Add bromine water in 1-ml portions until the yellow colour persists. Heat to boiling, adding more bromine water if the colour fades before the boiling point is reached. Boil off excess bromine, cool and add 1 ml of ammonium thiocyanate solution and 10 ml of the extraction solvent. Transfer the contents of each flask to a corresponding 50-ml graduated cylindrical separating funnel and shake for 15 seconds. Allow the two layers to separate and draw off the aqueous layer into the original conical flask. Wash the solvent layer with 1 ml of distilled water without mixing, draw off this wash water and add it to the water previously separated. Discard the solvent layer, return the water layer to the separating funnel and repeat the extraction using successive additions of 0·5 ml of ammonium thiocyanate solution and 5 ml of the extraction solvent until the solvent layer at the end of an extraction is practically colourless, washing the solvent

layer each time with 1 ml of distilled water and adding this to the water layer previously separated.

31.3.3 Add distilled water to each flask and bring the total volume to 25 ml and then add ammonium carbonate solution to adjust the *p*H of the solution to 7·5 ± 0·2. Add 10 ml of glycerine solution and 5 ml of hematoxylin solution to each flask, mix and allow to stand for 15 minutes. At this stage the colour varies from magenta in the blank through purple to almost pure blue in the other solutions, depending on aluminium concentration. Add 5 ml of ammonium borate solution and allow to stand until the magenta colour of the dyestuff fades out of each solution. About two minutes are usually sufficient. Transfer the solution from each flask to a corresponding Nessler tube and dilute to the mark. Compare the sample and blank with the prepared standards of known aluminium content.

31.4 Calculation

$$\text{Aluminium (as Al), mg/l} = \frac{1\,000\,A\,(V_1 - V_2)}{V_3}$$

where

A = amount in mg of aluminium in 1 ml of the standard aluminium solution,

V_1 = volume in ml of standard aluminium solution required to produce the colour matching that produced in the sample,

V_2 = volume in ml of standard aluminium solution required to produce the colour matching that produced in the blank, and

V_3 = volume in ml of the sample taken for the test.

31.5 Accuracy — Provided the amount of iron originally present is not more than 10 times the aluminium content, the values obtained by this method are accurate within the following limits:

Aluminium Content, mg/l	*Accuracy*, mg/l
0·01 to 0·1	0·01
0·1 ,, 0·5	0·05

32. IRON

32.0 Outline of the Method — The purple colour developed with thioglycollic acid in ammoniacal solution is matched against that obtained with a series of standard iron solutions.

32.1 Apparatus

32.1.1 *Nessler Tubes* — 50 ml capacity.

32.2 Reagents

32.2.1 *Potassium Bisulphate*

32.2.2 *Ammonium Hydroxide* — sp gr 0·92.

32.2.3 *Dilute Hydrochloric Acid* — 1 : 3 *v/v*.

32.2.4 *Thioglycollic Acid Reagent* — 10 percent *v/v*. Store in an amber bottle and discard after one month.

32.2.5 *Standard Iron Solution* — Dissolve 0·702 g of ferrous ammonium sulphate [$FeSO_4.(NH_4)_2SO_4.6H_2O$] in 100 ml of distilled water and 10 ml of concentrated sulphuric acid (conforming to Analytical Reagent Grade of IS : 266-1961*). Warm the solution and add N/8 potassium permanganate solution until the ferrous iron is oxidized as shown by the persistence of slight pink colour. Dilute to 1 000 ml. Before use, again dilute 25 ml of the solution to 250 ml. One millilitre of the final solution contains 0·01 mg of iron (as Fe).

32.3 Pre-treatment of Sample — The following types of pre-treatment are to be applied for the various forms of iron to be determined. The determination should be made as soon as possible after the sample is collected, especially for soluble iron. If the sample to be analysed for total iron is measured and acidified, it may be safely stored.

32.3.1 *Total Iron* — The sample is mixed thoroughly, measured and tested.

32.3.2 *Dissolved Iron* — Allow the sample to settle, then decant and filter through a fine filter paper, discarding the first portion.

32.4 Procedure — Evaporate a suitable volume of the sample containing not more than 0·2 mg of iron to dryness in a platinum dish and ignite gently to destroy the organic matter present. Fuse the ignited residue with potassium bisulphate, dissolve in distilled water and precipitate iron and aluminium with ammonium hydroxide. Filter, dissolve the precipitate in dilute hydrochloric acid, dilute the solution to about 30 ml with distilled water and add 2 ml of thioglycollic acid reagent followed by 2·5 ml of ammonium hydroxide. Transfer quantitatively to a Nessler tube and make up to 50 ml. Compare in Nessler tubes with the colour obtained with standard iron solutions treated in the same manner. Alternatively, compare the colour at 530 to 540 mμ.

32.5 Calculation

$$\text{Iron (as Fe), mg/l} = \frac{10\,V_1}{V_2}$$

*Specification for sulphuric acid (*revised*).

where

V_1 = volume in ml of standard iron solution present in the solution which matches the colour obtained with the sample, and

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

33. CALCIUM

33.0 General — Two alternate methods are prescribed for determination of calcium. The potassium permanganate method is described in **33.1** and ethylenediamine tetra-acetate (EDTA) method is described in **33.2**. In case of dispute, the permanganate method shall be used.

33.1 Potassium Permanganate Method

33.1.0 *Outline of the Method* — Calcium is precipitated as its oxalate and the precipitate, after dissolving it in sulphuric acid, is titrated with standard potassium permanganate solution.

33.1.1 *Reagents*

33.1.1.1 *Concentrated hydrochloric acid* — conforming to IS : 265-1962*.

33.1.1.2 *Bromine water* — saturated.

33.1.1.3 *Dilute ammonium hydroxide* — 1 : 4 *v/v*.

33.1.1.4 *Ammonium oxalate solution* — saturated.

33.1.1.5 *Dilute sulphuric acid* — approximately 6 N.

33.1.1.6 *Standard potassium permanganate solution* — 0·1 N.

33.1.2 *Procedure*

33.1.2.1 Measure 1 litre or a suitable volume of the sample and add concentrated hydrochloric acid until the sample is distinctly acid, and 1 ml in excess. Evaporate to about 100 ml in a borosilicate glass beaker. Transfer the solution to a silica or porcelain basin, evaporate to dryness and heat in a muffle furnace at 500° ± 25°C for about 10 minutes. Add to the residue 5 ml of concentrated hydrochloric acid and about 50 ml of distilled water, boil gently for 10 minutes and dilute to about 100 ml. Cool and add about 10 ml of bromine water and dilute ammonium hydroxide until the solution is faintly ammoniacal, and digest on a hot-plate for half an hour. Filter hot and wash the precipitate with hot water. Add concentrated hydrochloric acid until the solution is faintly acid. Boil to remove any bromine liberated. Add an excess of ammonium oxalate solution and make faintly ammoniacal. Maintain hot until the supernatant liquid is clear.

33.1.2.2 Filter off the precipitate on a sintered glass crucible (G No. 3). Wash the precipitate with warm water until free from chloride. Reserve

*Specification for hydrochloric acid (*revised*).

the filtrate for use in the determination of magnesium in **34**. To ensure complete recovery of magnesium, dissolve the precipitate by passing through the filter 5 ml of concentrated hydrochloric acid in about 30 ml of warm distilled water. Wash the filter with warm distilled water until the total volume is about 100 ml. Reprecipitate the calcium adding about 5 ml of ammonium oxalate solution before the addition of dilute ammonium hydroxide. Filter through the same crucible and wash with warm distilled water until free from chlorides. Add the filtrate to the previous filtrate and reserve for the determination of magnesium (*see* **34**).

33.1.2.3 Place the crucible with the precipitate in a beaker. Add about 100 ml of warm distilled water and 20 ml of dilute sulphuric acid. Heat to 60°C and titrate with standard potassium permanganate solution.

33.1.3 *Calculation*

a) Calcium (as Ca), mg/l $= \frac{2\,000\ V_1}{V_2}$

b) Calcium (as $CaCO_3$), mg/l $= \frac{5\,000\ V_1}{V_2}$

where

V_1 = volume in ml of standard potassium permanganate solution used in the titration, and

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

33.1.4 *Range* — The range of the method is up to 200 mg of calcium (as Ca).

33.2 EDTA Method

33.2.0 *Outline of the Method* — The sample is titrated against EDTA solution using murexide indicator.

33.2.1 *Reagents*

33.2.1.1 *Decolourizing powder* — Activated charcoal powder giving a blank of less than 0·5 mg/l in terms of calcium carbonate.

33.2.1.2 *Dilute hydrochloric acid* — Dilute 68 ml of concentrated hydrochloric acid to 100 ml with distilled water.

33.2.1.3 *Sodium hydroxide solution* — approximately 4 N.

33.2.1.4 *Murexide indicator* — Mix 0·20 g of murexide and 100 g of sodium chloride and grind to a fine powder.

33.2.1.5 *Standard calcium chloride solution* — Dissolve 1 g of calcium carbonate, accurately weighed, contained in a beaker covered with a watch-glass in a small amount of dilute hydrochloric acid. Wash down the beaker and watch-glass with carbon dioxide-free water, neutralize exactly with sodium hydroxide solution and make up to 1 litre with carbon dioxide-free water. One millilitre of the solution contains 1 mg of calcium carbonate.

33.2.1.6 *Standard sodium ethylenediamine tetra-acetate solution* (*EDTA solution*) — Dissolve 4·0 g of disodium ethylenediamine tetra-acetate dihydrate in approximately 800 ml of water. Add 5 ml of sodium hydroxide solution and 0·1 g of magnesium chloride ($MgCl_2.6H_2O$). Titrate against standard calcium chloride solution (10 ml diluted to 50 ml) as described under **33.2.2.2** and **33.2.2.3** and adjust so that 1 ml is equivalent to 1 mg of calcium carbonate ($CaCO_3$).

33.2.2 *Procedure*

33.2.2.1 If the colour of the sample is less than about 200 Hazen units (pale straw colour), it is possible to determine calcium as described in **33.2.2.2** or **33.2.2.3** without removal of colour. Otherwise, decolourization is necessary. In that case, add 1 g of decolourizing powder to 100 ml of distilled water containing 1 ml of dilute hydrochloric acid. Mix thoroughly and filter through a pad of paper pulp supported on a filter disc resting in a glass adapter. Use a Witts filter or similar apparatus and a moderate vacuum. Wash the bed of decolourizing powder with 100 ml of distilled water and discard the filtrate and washings. Take 500 ml (*see* Note) of the coloured sample which has been filtered until clear, and adjust the *p*H with dilute hydrochloric acid to 2·5 (a drop gives a yellow colour with bromophenol blue indicator). Filter through the bed of decolourizing powder, re-filtering if necessary, until the colour is satisfactory.

NOTE — When the calcium content (as $CaCO_3$) is greater than 10 mg/l, 100 ml of the sample may be used.

33.2.2.2 *For calcium content up to 10 mg/l (as $CaCO_3$)* — To 500 ml of the sample contained in a large porcelain dish, add 5 ml of sodium hydroxide solution and 0·6 g of murexide indicator. Titrate with standard EDTA solution until the solution becomes violet. It is found that the end point is best indicated when a further addition of 0·1 ml of standard EDTA solution produces no further colour change.

33.2.2.3 *For calcium content greater than 10 mg/l (as $CaCO_3$)* — Transfer 100 ml (*see* Note) of the sample to a porcelain dish, add 1 ml of sodium hydroxide solution and 0·2 g of murexide indicator. Titrate as in **33.2.2.2**.

NOTE — When calcium content of the sample is greater than 250 mg/l (as $CaCO_3$), use 50 ml or less of the sample.

33.2.3 *Calculation*

a) Calcium (as Ca), mg/l $= \dfrac{400\ V_1}{V_2}$

b) Calcium (as $CaCO_3$), mg/l $= \dfrac{1\,000\ V_1}{V_2}$

where

V_1 = volume in ml of standard EDTA solution used in the titration, and

V_2 = volume in ml of the sample taken for the titration.

33.2.4 *Range* — The method may be used in the range 0·1 to 25 mg of calcium carbonate.

34. MAGNESIUM

34.0 General — Three alternate methods are prescribed for the determination of magnesium, namely the pyrophosphate method, the oxine method and the titan yellow method. In addition, a simple method for calculating magnesium content from total hardness and calcium content is given in **34.4**. Since the method given in **34.4** is a method using difference of calculated results, the accuracy is reduced when the magnesium/calcium ratio in the sample is low.

34.1 Pyrophosphate Method

34.1.0 *Outline of the Method* — Magnesium is precipitated as its phosphate and the precipitate ignited and weighed as magnesium pyrophosphate.

34.1.1 *Reagents*

34.1.1.1 *Dilute hydrochloric acid* — 4 N approximately.

34.1.1.2 *Ammonium phosphate solution* — 10 percent *w/v*.

34.1.1.3 *Methyl red indicator* — Dissolve 0·1 g of methyl red in 100 ml of rectified spirit conforming to IS : 323-1959*.

34.1.1.4 *Ammonium hydroxide* — 4 N and 1 N approximately.

34.1.2 *Procedure* — Neutralize the combined filtrate and washings preserved in **33.1.2.2** and make it slightly acidic with dilute hydrochloric acid. Dilute the solution so as to contain not more than 0·1 g of magnesium oxide per 100 ml and for each 100 ml of solution add 20 ml of ammonium phosphate solution. Add 2 to 3 drops of methyl red indicator. Stir vigorously for about 10 minutes, and then add, while stirring, ammonium hydroxide (4 N) dropwise till the acid is neutralized, followed by further addition of 20 ml of ammonium hydroxide (4 N). Continue stirring for 15 minutes more and allow to settle for at least 4 hours (preferably overnight). Filter and wash the precipitate with ammonium hydroxide (1 N) till free from phosphate. Place the filter paper along with the precipitate in a tared crucible, dry in an oven and char the filter paper by gentle heating over a low flame; gradually raise the temperature and finally ignite at 1 000°C to constant weight.

34.1.3 *Calculation*

$$\text{Magnesium (as Mg), mg/l} = 218\,500\,\frac{w}{v}$$

where

w = weight in g of the precipitate obtained, and

v = volume in ml of the sample taken for the test in **33.1.2.1**.

*Specification for rectified spirit (*revised*).

34.1.4 *Precision and Accuracy* — The method is precise to ±0·5 mg or better, and the accuracy is comparable if interferences are absent.

34.2 Oxine Method

34.2.0 *Outline of the Method* — Magnesium is precipitated, with proper *p*H control, with 8-hydroxyquinoline and weighed as magnesium oxinate (hydrated or anhydrous).

34.2.1 *Reagents*

34.2.1.1 *Ammonium chloride*

34.2.1.2 *o-Cresolphthalein indicator solution* — 0·2 percent solution in rectified spirit conforming to IS : 323-1959*.

34.2.1.3 *Ammonium hydroxide* — 6 N approximately.

34.2.1.4 *Oxine solution* — Dissolve 2 g of reagent grade oxine (8-hydroxyquinoline) in 100 ml of 2 N acetic acid. Add ammonium hydroxide dropwise until turbidity begins to form. Clarify the solution by adding a little acetic acid.

34.2.1.5 *Dilute ammonium hydroxide* — 1 : 40 *v/v*.

34.2.2 *Procedure* — To the combined filtrate and washings preserved in **33.1.2.2** and adjusted to 100 ml, add 2 g of ammonium chloride and 0·5 ml of *o*-cresolphthalein indicator. Neutralize with ammonium hydroxide until a violet colour is obtained (*p*H about 9·5) and then add 2 ml of ammonium hydroxide in excess. Heat to 70° to 80°C, add very slowly and with constant stirring oxine solution until a small excess is present as shown by the deep yellow colour of the supernatant liquid. Avoid a large excess of the precipitant. Digest the precipitate on a steam-bath for half an hour with frequent stirring and collect the precipitate on a weighed sintered glass (G No. 3) or Gooch crucible. Wash the precipitate with dilute ammonium hydroxide, dry to constant weight at 100° to 110°C and weigh as $Mg(C_9H_6ON)_2.2H_2O$. Alternatively, the precipitate may be dried at 155° to 160°C and weighed as the anhydrous compound $Mg(C_9H_6ON)_2$.

34.2.3 *Calculation*

$$\text{Magnesium (as Mg), mg/l} = \frac{69\,760\,w_1}{v} \text{ or } \frac{77\,800\,w_2}{v}$$

where

w_1 = weight in g of the precipitate dried at 100° to 110°C,

w_2 = weight in g of the precipitate dried at 155° to 160°C, and

v = volume in ml of the sample taken for the test in **33.1.2.1**.

*Specification for rectified spirit (*revised*).

34.2.4 *Range* — The method may be used in the range 0·5 to 30 mg of magnesium (as Mg).

34.3 Titan Yellow Method

34.3.0 *Outline of the Method* — Magnesium gives a colour with titan yellow in the presence of calcium and starch solution. The colour produced is measured in an absorptiometer.

34.3.1 *Reagents*

34.3.1.1 *Dilute hydrochloric acid* — 0·1 N approximately.

34.3.1.2 *Calcium chloride solution* — Weigh 5·000 g of calcium carbonate and add to it about 100 ml of distilled water. Dissolve the calcium carbonate by addition of 100 ml of hydrochloric acid (1 N) and dilute to 500 ml. Dilute 100 ml of the solution again to 500 ml. One millilitre of the solution is equivalent to 2 mg of calcium carbonate.

34.3.1.3 *Standard magnesium solution* — Dissolve 2·432 4 g of magnesium sulphate ($MgSO_4.7H_2O$) in about 200 ml of distilled water, add 2 ml of concentrated hydrochloric acid and dilute to 1 litre. Dilute 50 ml of this solution again to 1 litre with distilled water. One millilitre of the solution is equivalent to 12 μg of magnesium (as Mg). Keep the solution in a polyethylene bottle.

34.3.1.4 *Starch solution* — Mix 1 g of soluble starch with 5 ml of cold distilled water, then add 95 ml of boiling water. Heat to boiling and cool. Store in a glass bottle in the dark. Prepare fresh every five days. Filter immediately before use through a filter paper (Whatman No. 41 or equivalent) .

34.3.1.5 *Titan yellow solution* — Dissolve 0·15 g of titan yellow in 400 ml of cold distilled water. Filter off any insoluble matter on a sintered glass crucible (G No. 3) using suction. Wash with a little distilled water and dilute the filtrate to 500 ml.

NOTE — Since different batches of titan yellow give different levels of optical density readings for equivalent amounts of magnesium, it is essential to prepare a fresh calibration curve for each new batch of titan yellow.

34.3.1.6 *Standard sodium hydroxide solution* — 1 N, prepared from carbonate-free sodium hydroxide and carbon dioxide-free distilled water. Keep in a polyethylene bottle and do not use for more than two weeks after preparation.

34.3.1.7 *Standard potassium dichromate solution* — 0·02 N.

34.3.2 *Procedure*

34.3.2.1 Measure accurately a volume of the sample containing not more than 180 μg of magnesium (*see* Note). Adjust the volume of sample taken to 25 ml by evaporation or by dilution with distilled water. Transfer to a 50-ml graduated flask, neutralize to methyl orange with the required

amount of dilute hydrochloric acid as determined by a separate titration and add a further 2 ml of the acid. Add calcium chloride solution to adjust the calcium content to the equivalent of 20 mg of calcium carbonate. The presence of calcium chloride intensifies the colour of the complex of titan yellow and magnesium, and therefore, the amount of calcium is kept constant.

NOTE — If more than 12 µg of aluminium is present in the portion taken for test, remove the aluminium as follows:

Measure 250 ml of the sample and transfer to a 400-ml beaker. Add 5 ml of hydrochloric acid (sp gr 1·18) and a volume of a standard iron solution containing 1·5 mg of iron. Oxidize any ferrous iron by addition of 1 ml of bromine water, heat the solution to boiling and continue boiling until the volume is reduced to approximately 100 ml. Then add 2 drops of methyl red indicator followed by dropwise addition of ammonia (sp gr 0·92) until the solution changes to yellow, add 2 drops of ammonia (sp gr 0·92) in excess and continue boiling for one minute. Place the beaker containing the solution on a steam-bath for 15 minutes in order to coagulate the precipitate. Filter the solution through a 9-cm filter paper (Whatman No. 40 or equivalent) and wash four times with 10-ml portions of hot water; collect the filtrate and washings in a 250-ml graduated flask. Cool the contents of the flask to room temperature, acidify by addition of a few drops of hydrochloric acid (sp gr 1·18) then dilute with distilled water to the graduation mark, and mix thoroughly.

Measure accurately a volume of this solution containing not more than 180 µg of magnesium and transfer to a silica dish; evaporate the solution to dryness on a steam-bath and then heat in an oven at 105 to 120°C for 30 minutes to ensure complete dryness of the residue. Heat the dried residue to remove ammonium salts; then allow to cool. To the residue, add sufficient calcium chloride solution to give a content of calcium equivalent to 20 mg of calcium carbonate; and dilute hydrochloric acid to give an overall excess of 2 ml and sufficient distilled water to bring the volume to about 10 ml. Cover the dish with a watch-glass and digest on a steam-bath for 10 minutes, then filter through a 7-cm filter paper (Whatman No. 40 or equivalent) and wash with small volumes of warm water until a total volume of approximately 25 ml is obtained. Cool the solution; collect the filtrate and washings in a 50-ml graduated flask. Determine the magnesium as in **34.3.2.2** and **34.3.2.3**.

34.3.2.2 Add 1·0 ml of standard magnesium solution (*see* Note 1), 3·0 ml of starch solution and 4·0 ml of titan yellow solution in this order. Mix well after each addition, then dilute to approximately 45 ml. Place the flask containing the solution in a bath thermostatically controlled at 20·0 ± 0·1°C for 30 minutes (*see* Note 2). At the end of this time, add 3·0 ml of standard sodium hydroxide solution and mix during the addition by gently swirling the flask. Dilute to 50 ml, mix thoroughly and allow to stand in the bath for a further 15 minutes. Measure the optical density in a photoelectric absorptiometer using a 4-cm cell and a blue-green filter transmitting between 4 700 and 5 200 Å approximately. Place standard potassium dichromate solution in the comparison cell (*see* Note 3).

NOTE 1—Amounts of magnesium below 12 µg do not give a linear relationship between the optical density and the amount of magnesium present. For this reason 12 µg of magnesium is always added to the sample, to the blank, and to the magnesium solutions used in preparing the calibration curve.

NOTE 2 — The colour development is carried out at 20·0 ± 0·1°C but a higher temperature may be used provided that all calibrations are carried out at the higher temperature and this temperature is controlled within narrow limits.

NOTE 3 — The use of 0·02 N potassium dichromate in the comparison cell when using an absorptiometer enables readings to be taken at the lower (more sensitive) end of the scale.

34.3.2.3 For a blank determination, measure into a 50-ml measuring flask 10 ml of calcium chloride solution and 2 ml of dilute hydrochloric acid. Dilute to 25 ml and proceed as described above for the test solution, commencing at **34.3.2.2**. Deduct the reading of the blank from that obtained with the sample and from the difference ascertain the amount of magnesium present, using a graph previously prepared by plotting readings obtained with known amounts of magnesium using the method described above for the test solution.

34.3.3 *Calculation*

$$\text{Magnesium (as Mg), mg/l} = \frac{W}{V}$$

where

W = amount in µg of magnesium corresponding to the optical density obtained with the sample, and

V = volume in ml of the sample taken for the test.

34.3.4 *Range* — The method is applicable up to 180 µg of magnesium (as Mg).

34.4 Calculation of Magnesium Content from Total Hardness and Calcium Content

$$\text{Magnesium (as Mg), mg/l} = 0{\cdot}2430 \,[\, \text{total hardness (as } CaCO_3 \text{ mg/l)} - \text{calcium content (as } CaCO_3 \text{ mg/l)} \,]$$

35. MANGANESE

35.0 Outline of the Method — The manganese in the sample is oxidized with potassium periodate. The pink colour obtained is matched against that produced with a series of standard manganese solutions.

35.1 Apparatus

35.1.1 *Nessler Tubes* — 50 ml capacity.

35.2 Reagents

35.2.1 *Dilute Sulphuric Acid* — 1 : 1 *v/v*.

35.2.2 *Hydrogen Peroxide — Nitric Acid Mixture* — Mix equal volumes of hydrogen peroxide (30 percent) and concentrated nitric acid. Prepare fresh every day.

35.2.3 *Stabilized Distilled Water* — Assemble a distillation apparatus consisting of a round bottom 1-litre flask fitted with an efficient splash head, connected to a Liebig condenser by means of ground-glass joints. Introduce 500 to 600 ml of distilled water into the flask, add about 0·1 g of potassium permanganate previously dissolved in 5 ml of water and a few drops of dilute sulphuric acid. Distil carefully taking care that there is no carryover by splashing or otherwise of liquid from the flask, and reject the first 50 ml of distillate.

35.2.4 *Phosphoric Acid* — sp gr 1·75.

35.2.5 *Potassium Periodate*

35.2.6 *Standard Manganese Solution* — Measure 45·5 ml of 0·1 N potassium permanganate solution into a 250-ml beaker, add a few drops of dilute sulphuric acid, heat to boiling and then add a saturated solution of sulphur dioxide in water drop by drop until the permanganate is just decolourized. Boil for 15 minutes, cool, transfer the solution to a 500-ml graduated flask, dilute to the mark and mix well. Measure 100 ml of the solution into a 500-ml graduated flask, add 5 ml of dilute sulphuric acid, dilute to the mark and mix well. One millilitre of the diluted solution is equivalent to 0·02 mg of manganese (as Mn).

35.3 Procedure — Into a 300-ml conical flask of borosilicate glass measure a suitable volume of the well mixed sample (*see* Note). Add 4·0 ml of dilute sulphuric acid and evaporate to fuming. Whilst heating, treat with the hydrogen peroxide-nitric acid mixture, adding a few drops at a time, until all traces of organic matter are completely destroyed. Cool, add 10 ml of stabilized distilled water and evaporate to fuming; again cool and repeat the addition of water followed by evaporation. Add 50 ml of stabilized distilled water, 2 ml of the phosphoric acid and 0·2 g of potassium periodate, bring to the boil and keep just below the boiling point for one hour. Cool to room temperature, transfer the solution to a Nessler tube, adjust the volume to 50 ml with stabilized distilled water and mix well. Into seven 300-ml conical flasks measure by means of a burette, 0, 1·0, 2·0, 4·0, 6·0, 8·0 and 10 ml of standard manganese solution. Treat as described above for the sample. Transfer the solutions to Nessler tubes, dilute to the mark with stabilized distilled water and mix. Compare the colours of the sample and standards.

NOTE — Suitable volumes of sample are as follows:

Calcium Content of Sample as $CaCO_3$	*Volume of Sample*
mg/l	ml
Up to and including 250	200
251 to 500	100
501 „ 1 000	50

35.4 Calculation

$$\text{Manganese (as Mn), mg/l} = 1\,000\,\frac{W}{V}$$

where

W = amount in mg of manganese present in the standard which matches the colour obtained with the sample, and

V = volume in ml of the sample taken for the test.

35.5 Range — The method is applicable up to 0·2 mg of manganese (as Mn).

36. COPPER

36.0 Outline of the Method — The yellow colour obtained with diethyldithiocarbamate in ammoniacal solution is matched against that produced with a series of standard copper solutions.

36.1 Apparatus

36.1.0 All glassware to be used in the test shall first be rinsed with concentrated hydrochloric acid and then with redistilled water (*see* **36.2.1**).

36.1.1 *Nessler Tubes* — 100 ml capacity.

36.2 Reagents

36.2.1 *Redistilled Water* — Water redistilled from an all-glass pyrex still.

36.2.2 *Dilute Ammonium Hydroxide* — 1 : 5 *v/v*.

36.2.3 *Diethyldithiocarbamate Solution* — Dissolve 1 g of sodium diethyldithiocarbamate in 1 litre of redistilled water. A brown bottle is recommended for the solution. The reagent becomes turbid in approximately a month. A reagent which has become coloured should be discarded but slight turbidity may be tolerated.

36.2.4 *Standard Copper Solution* — Weigh 0·100 0 g of copper metal foil, place in a 250-ml beaker under a hood, add 3 ml of redistilled water and 3 ml of concentrated nitric acid, and cover the beaker with a watch-glass. After the metal has all dissolved, add 1 ml of concentrated sulphuric acid and heat on a hot-plate to volatilize the acids. Stop heating just short of complete dryness; do not bake the residue. Cool and dissolve in redistilled water, washing down the sides of the beaker and the bottom of the watch-glass. Transfer quantitatively to a 1-litre volumetric flask and make up to the mark with redistilled water. Quantitatively dilute 50 ml of the solution to 1 litre with redistilled water. One millilitre of this solution contains 0·005 mg of copper (as Cu). This solution is stable indefinitely.

36.3 Procedure — To 100 ml of the sample, or an aliquot diluted to 100 ml with redistilled water, taken in a Nessler tube, add 5 ml of dilute ammonium hydroxide and 5 ml of diethyldithiocarbamate solution. Mix by inverting the tube twice. Simultaneously, take in a series of Nessler tubes, 0·0, 1·0, 2·0, 4·0, 8·0, 12·0, 16·0 and 20·0 ml of standard copper solution, dilute to 100 ml with redistilled water and treat as described above for the sample. Compare the yellow colour obtained with the sample with that obtained with the standards after 5 minutes but within one hour of mixing.

NOTE — Extraction procedures have been recommended by various authors. Carbon tetrachloride add *iso*amyl alcohol have been used for extracting and, thereby to intensify the colour and/or to eliminate turbidity. The solvents are added after the colour has developed. The mixtures are then shaken to cause the colour to pass into the organic layer. Care shall be taken that the solvents themselves do not contain traces of metals. It is desirable to acidify the aqueous solution immediately prior to the extraction which is slow from an alkaline solution.

36.4 Calculation

$$\text{Copper (as Cu), mg/l} = 1\,000\,\frac{W}{V}$$

where

W = weight in mg of copper present in the standard which matches the colour obtained with the sample, and

V = volume in ml of the sample taken for the test.

36.5 Precision and Accuracy — The minimum detectable amount of copper is 0·05 mg/l. A precision of ±6 percent may be achieved.

37. LEAD

37.0 Outline of the Method — The red colour obtained with dithizone is matched against that produced with a series of standard lead solutions.

37.1 Apparatus

37.1.0 *General* — Lead-free borosilicate glass shall be used in the test.

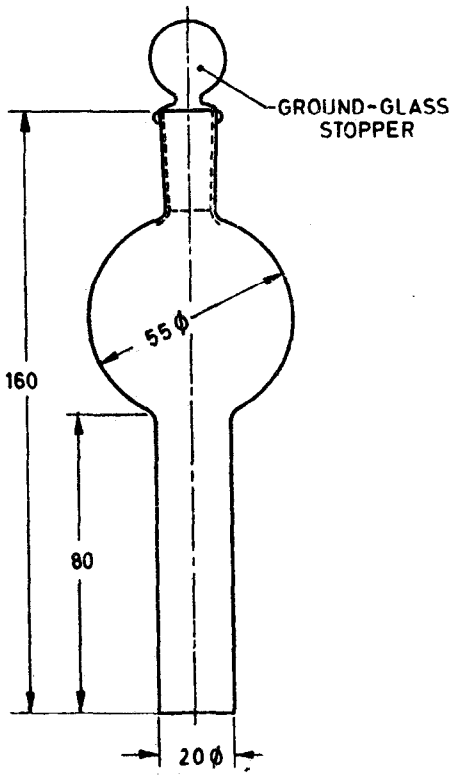
37.1.1 *Titration Flasks* — as shown in Fig. 2.

37.2 Reagents

37.2.1 *Methyl Orange Indicator* — Dissolve 0·1 g of methyl orange in 100 ml of rectified spirit.

37.2.2 *Concentrated Nitric Acid* — Redistil concentrated nitric acid in an all-glass distillation apparatus.

37.2.3 *Dilute Nitric Acid* — 20 percent and 1 percent *v/v*, prepared from concentrated nitric acid.



All dimensions in millimetres.

FIG. 2 TITRATION FLASK

37.2.4 *Dilute Ammonium Hydroxide* — 10 N.

37.2.5 *Chloroform* — Redistilled in an all-glass distillation apparatus.

37.2.6 *Hydroxylamine Hydrochloride Solution* — Prepare a 10 percent *w/v* solution in water. Add 2 drops of phenol red indicator, make slightly alkaline with ammonium hydroxide and extract with a solution of dithizone in chloroform (approximately 0·01 percent) in slight excess, remove the excess dithizone with chloroform, evaporate the excess of chloroform, cool and filter.

37.2.7 *Sodium Citrate Solution* — Dissolve 147 g of trisodium citrate ($Na_3C_6H_5O_7.2H_2O$) in water and dilute to 500 ml. Add 3 drops of dilute ammonium hydroxide and extract with a solution of dithizone in chloroform (approximately 0·01 percent) in slight excess; remove the excess dithizone with chloroform, evaporate the excess of chloroform, cool and filter.

37.2.8 *Thymol Blue Indicator* — Dissolve 0·1 g of thymol blue in 100 ml of rectified spirit.

37.2.9 *Dilute Hydrochloric Acid* — Dilute concentrated hydrochloric acid with an equal volume of water and distil in an all-glass distillation apparatus.

37.2.10 *Dithizone, Purified* — Dissolve 1 g of dithizone in chloroform, filter, and shake the filtered solution contained in a 250-ml separating funnel with four successive 100-ml portions of ammonium hydroxide (1·0 percent *v/v*). Combine the orange coloured aqueous solutions, filter through a filter paper into a beaker and precipitate the dithizone from the filtrate by rendering it slightly acid with dilute hydrochloric acid. After settling, filter off the precipitate on a clean sintered glass crucible (G No. 3) using suction, and wash acid-free with distilled water. Dry the well-drained precipitate over sulphuric acid in vacuum for 3 to 4 days, protecting the material from light. The purified solid so prepared, when stored in the dark, is stable for at least six months.

37.2.11 *Dithizone Solution* — Prepare two solutions of dithizone in chloroform of strengths 30 mg/l and 8 mg/l, by dissolving the required weight of purified dithizone in a suitable volume of chloroform. The solution remains stable for at least one month if stored in a refrigerator. If stored at room temperature in the dark, it is stable for about one week.

37.2.12 *Potassium Cyanide Solution* — Dissolve 50 g of potassium cyanide in the minimum amount of water, transfer to a separating funnel, dilute to 100 ml and extract with 5-ml portions of dithizone solution (30 mg/l) to each of which has been added 5 ml of chloroform, until the last extract remains green and the aqueous layer is tinged yellow. Extract the excess of dithizone with 10-ml portions of chloroform until the final chloroform extract is colourless, and dilute the extracted cyanide solution to 500 ml with water.

37.2.13 *Strong Ammoniacal Potassium Cyanide Solution* — Measure a volume of dilute ammonium hydroxide to contain 38·3 g of ammonia (NH_3) into a 1-litre graduated flask, add 200 ml of potassium cyanide solution and dilute to 1 litre.

37.2.14 *Dilute Ammoniacal Potassium Cyanide Solution* — Measure 4 ml of dilute ammonium hydroxide and 1 ml of potassium cyanide solution into a 100-ml graduated flask and dilute to the mark.

37.2.15 *Standard Lead Solution* — Dissolve 0·160 g of lead nitrate, dried at 100°C, in 50 ml of water and 10 ml of concentrated nitric acid and dilute to 1 000 ml in a graduated flask. Measure 10·0 ml of this solution into a 500-ml graduated flask, add 9 ml of concentrated nitric acid, dilute to the mark with water and mix well. One millilitre of the diluted solution contains 0·002 mg of lead (as Pb).

37.3 Procedure

37.3.1 Measure 250 ml of the sample into a 500-ml beaker, add 2 drops of methyl orange indicator, just acidify with concentrated nitric acid and add 4 ml of the acid in excess. Boil down to a volume of 10 to 15 ml and transfer the solution to a small glass dish, using the minimum amount of distilled water. Evaporate to dryness on a steam-bath. Wash down the sides of the dish with 2 ml of concentrated nitric acid and again evaporate to complete dryness on a steam-bath. Transfer the dish to an electrically heated muffle furnace controlled at a temperature of 490 to 500°C and ignite for 20 minutes. Allow to cool, add 3 ml of concentrated nitric acid and 15 ml of distilled water and heat for 5 minutes on a steam-bath. Filter through a small filter paper (Whatman No. 40 or equivalent), wash with small amounts of hot dilute nitric acid (20 percent) and cool. Add 2 ml of hydroxylamine hydrochloride solution, 2 ml of sodium citrate solution and two drops of thymol blue indicator. Add dilute ammonium hydroxide until the indicator colour changes to full blue; cool again. The solution should be quite clear at this point; if not, re-acidify and increase the amount of sodium citrate. Add 1 ml of dilute ammonium hydroxide in excess and 1 ml of potassium cyanide solution.

37.3.2 Transfer the solution to a separating funnel and extract the lead by shaking with successive portions of 5 ml, 5 ml and 3 ml of dithizone solution (30 mg/l). If the last extract shows any pink colour, continue to extract with 3-ml portions until two consecutive extracts remain green. Collect the chloroform extracts in a second separating funnel, reject the aqueous layer and wash out the funnel in which it was contained. Wash the chloroform extract with 50 ml of distilled water, run the chloroform layer into the first funnel and wash the water layer with two 5-ml portions of chloroform, adding these chloroform washes to the main chloroform extract of lead dithizonate. Remove the lead from the combined chloroform solution by shaking for one and a half minutes with 20 ml of dilute nitric acid (1 percent). Reject the chloroform layer, washing the nitric acid layer with a little chloroform. Transfer the nitric acid solution of lead to a 25-ml graduated flask and dilute to the mark with dilute nitric acid (1 percent). Measure into the titration flask such a portion of this solution as will contain 10 to 15μg of lead and dilute to 25 ml with dilute nitric acid (1 percent), add 3 ml of strong ammoniacal potassium cyanide solution followed by 10·0 ml of dithizone solution (8 mg/l), and shake this mixture for 1 minute.

37.3.3 Prepare the standard by transferring 20 ml of dilute nitric acid (1 percent), 5 ml of standard lead solution, 4 ml of strong ammoniacal potassium cyanide solution and 10 ml of dithizone solution (8 mg/l) to a titration flask, and shaking for 1 minute. Compare the colour of the chloroform layer of the test sample with that of the standard, and then add standard lead solution to the solution with the lower lead content, that is, the greener solution until, after shaking and allowing to separate,

the colours of the two chloroform extracts match. Add or subtract, as required, this added volume to or from 5·0 ml to obtain the volume of lead solution equivalent to the lead present in the portion of the test solution taken.

37.3.4 Carry out a blank in a similar manner on all the reagents and apply the necessary correction.

37.4 Calculation

$$\text{Lead (as Pb), mg/l} = 1\,000\frac{W}{V}$$

where

W = weight in mg of lead equivalent to the lead content of the sample, and

V = volume in ml of the sample taken for the test.

37.5 Range — The method is applicable up to 0·03 mg/l of lead (as Pb).

38. CHROMIUM

38.0 Outline of the Method — Hexavalent chromium develops a violet colour with diphenyl carbazide in slightly acid solution. For determination of total chromium, the sample is oxidized with ammonium persulphate. The violet colour obtained is matched against that produced with a series of standard chromium solutions.

38.1 Apparatus

38.1.1 *Nessler Tubes* — 100 ml capacity.

38.2 Reagents

38.2.1 *Dilute Sulphuric Acid* — Add 50 ml of concentrated sulphuric acid to 50 ml of water and cool.

38.2.2 *Diphenyl Carbazide Solution* — Dissolve 0·2 g of diphenyl carbazide in 100 ml of rectified spirit (conforming to IS : 323-1959*) and add 400 ml of sulphuric acid (10 percent *v/v*). If kept under refrigeration, the solution is stable for about one month. Its colour will change from colourless to tan without affecting its usefulness.

38.2.3 *Standard Chromium Solution* — Dissolve 0·374 g of potassium chromate in distilled water and make up to 1 litre. Before use, dilute 10 ml of the solution to 1 litre. One millilitre of the diluted solution contains 0·001 mg of chromium (as Cr).

*Specification for rectified spirit (*revised*).

38.2.4 *Sodium Sulphite*

38.2.5 *Silver Nitrate Solution* — 5 percent, aqueous.

38.2.6 *Ammonium Persulphate Solution* — 10 percent, aqueous.

38.2.7 *Concentrated Hydrochloric Acid* — conforming to IS : 265-1962*.

38.2.8 *Sodium Carbonate*

38.3 Procedure

38.3.1 *For Hexavalent Chromium* (Cr^{6+}) — Place 50 ml of the sample in a Nessler tube, add 10 ml of dilute sulphuric acid and 5 ml of diphenyl carbazide solution. Allow to stand for 5 minutes but not more than 20 minutes and match the violet colour developed against a series of control standards prepared from standard chromium solution.

38.3.2 *For Total Chromium* — Evaporate 100 ml of the sample to dryness with 0·1 g of sodium sulphite in a platinum basin. Add 0·5 ml of dilute sulphuric acid and 1 ml of distilled water and heat until white fumes are given off. Dissolve the residue in 40 ml of distilled water. Add 1 ml of silver nitrate solution, 4 drops of concentrated nitric acid and heat to boiling. Add 10 ml of ammonium persulphate solution and boil for 10 minutes. If the sample contains manganese, add two drops of concentrated hydrochloric acid. Cool, transfer to Nessler tube and neutralize by addition of sodium carbonate. When neutral, add 10 ml of dilute sulphuric acid, make the volume up to 60 ml and add 5 ml of diphenyl carbazide solution. Match after 5 minutes but in any case not more than 20 minutes, the violet colour produced against a series of control standards prepared from standard chromium solution under identical conditions.

38.4 Calculation

a) Hexavalent chromium (as Cr), mg/l $= \frac{v_1}{v}$

b) Total chromium (as Cr), mg/l $= \frac{v_2}{v}$

where

v_1 = volume in ml of standard chromium solution present in the control standard which matches the colour obtained with the sample in **38.3.1**.

v_2 = volume in ml of standard chromium solution present in the control standard which matches the colour obtained with the sample in **38.3.2**, and

v = volume in ml of the sample taken for the test.

*Specification for hydrochloric acid (*revised*).

38.5 Range — The method is applicable in the range 0·1 to 10·0 mg/l of chromium (as Cr).

39. ZINC

39.0 Outline of the Method — The sample is evaporated to dryness and the residue ignited and dissolved in dilute acid. The solution is extracted with carbamate at *p*H 7·5 to 8 and the carbamate extract again shaken with alkaline sodium citrate solution. The aqueous extract, after adjustment of *p*H, is titrated against dithizone reagent.

39.1 Reagents

39.1.1 *Dilute Hydrochloric Acid* — approximately 5 N and 1 N.

39.1.2 *Chloroform* — redistilled in an all-glass distillation apparatus.

39.1.3 *Ammonium Hydroxide* — 10 N approximately.

39.1.4 *Dithizone Stock Solution* — 0·1 percent solution in chloroform.

39.1.5 *Sodium Citrate Solution* — Dissolve 150 g of trisodium citrate in water and dilute the solution to 500 ml. Remove the zinc from this solution as follows. Transfer it to a large separating funnel, make it slightly ammoniacal and shake it thoroughly with addition of dithizone stock solution until the last extract remains green and the aqueous layer becomes slightly yellow. Then add 2 ml of citric acid solution (20 percent *w/v*) and extract the whole with successive portions of chloroform until the last extract is colourless.

39.1.6 *Bromothymol Blue Indicator Solution* — Dissolve 0·1 g of bromothymol blue in 100 ml of rectified spirit.

39.1.7 *Carbamate Extraction Reagent* — Dilute 1 ml of redistilled carbon disulphide to 10 ml with dry chlroform and add this mixture slowly, with stirring and cooling, to 3 ml of redistilled diethylamine diluted to 10 ml with dry chloroform. Preserve the solution in a glass-stoppered amber-coloured bottle. It shall be prepared about once a week. Dilute 5 ml of the above solution to 100 ml with chloroform and keep the solution in a glass-stoppered bottle. The dilution shall be done when required.

39.1.8 *Alkaline Citrate Solution* — Mix together 50 ml of sodium citrate solution, 100 ml of sodium hydroxide solution (10 percent *w/v*) and 100 ml of distilled water.

39.1.9 *Bromine Water* — saturated.

39.1.10 *Sodium Metabisulphite Solution* — 5 percent, aqueous.

39.1.11 *Buffer Solution* — Dissolve 30 g of borax in distilled water and dilute to 1 litre. Remove interfering metals by extraction with dithizone

stock solution and then remove the last traces of dithizone by repeated extraction with chloroform.

39.1.12 *Dithizone Reagent* — Extract 40 ml of dithizone stock solution with two 50-ml portions of dilute ammonium hydroxide (50 ml of distilled water containing 2 ml of ammonium hydroxide) and reject the chloroform layer. Acidify the combined ammoniacal extracts with dilute hydrochloric acid (5 N) and extract with 100 ml of chloroform. Wash the extract with two 10-ml portions of distilled water and filter through a dry paper. Prepare this solution every day. It is convenient that 1 ml of this solution should be equivalent to about 20 to 25 µg of zinc and a preliminary standardization for this purpose is desirable.

39.1.13 *Standard Zinc Solution* — Dissolve 1·000 g of pure zinc in 5 ml of concentrated hydrochloric acid and 10 ml of distilled water. Transfer the solution to a 1-litre graduated flask, dilute to the mark and mix well. Transfer 10 ml of the solution to a 1-litre graduated flask, add 5 ml of dilute hydrochloric acid (1 N) and dilute to the mark. One millilitre of the diluted solution is equivalen to 0·01 mg of zinc (as Zn). The diluted solution shall be prepared daily as required.

39.2 Procedure

39.2.1 Measure 500 ml of the sample into a 1-litre glass beaker, neutralize with dilute hydrochloric acid (5 N) and add 2 ml of the acid in excess. Boil down to about 20 ml, transfer to a platinum dish, and evaporate to dryness on a steam-bath. Gently ignite to destroy organic matter and allow to cool. Add 5 ml of dilute hydrochloric acid (5 N) gradually down the sides of the dish. Moisten all the residue with the acid, cover with a clock-glass and heat on a steam-bath or hot-plate for 15 to 20 minutes. Add 10 ml of distilled water, stirring to dissolve the residue. Small amounts of silica and possibly a little carbonaceous matter may remain. Filter into a 100-ml beaker or conical flask, wash with small amounts of dilute hydrochloric acid (1 N) and reject the residue. To the filtrate, add 5 ml of sodium citrate solution and 0·2 ml of bromothymol blue indicator and almost neutralize with ammonium hydroxide and cool. Continue the addition of ammonium hydroxide until the indicator just changes to full blue (*p*H 7·5 to 8·0). Transfer the solution to a separating funnel and extract it with 15 ml of carbamate extraction reagent, shaking it vigorously for 40 seconds. Run off the lower layer into a second separating funnel and extract the aqueous layer further with 5 ml of chloroform, shaking for 45 seconds; add the chloroform layer to the first extract and reject the aqueous layer.

39.2.2 Add to the chloroform extract 15 ml of alkaline citrate solution and shake the mixture for 40 seconds. Allow the chloroform layer to separate completely, then carefully run it off and reject it. Shake the aqueous layer with 5 ml of chloroform for about 10 seconds. Run off and reject the chloroform layer. Drain the aqueous solution into a beaker or conical

flask, rinsing the funnel with a little distilled water. Add 0·2 ml of bromothymol blue indicator. Add dilute hydrochloric acid (5 N) until the colour of the indicator changes from blue to yellow and then 4 ml in excess. In order to destroy diethylammonium diethyldithiocarbamate, add 10 ml of bromine water and boil carefully until the solution is nearly colourless. Add 0·5 ml of sodium metabisulphite solution and cool to room temperature. Call this the *test solution*. The whole of the *test solution* may be titrated or it may be made up to a definite volume (say 100 ml) for titration of a suitable aliquot portion.

39.2.3 Transfer the whole, or an aliquot portion, of the *test solution* to a 250-ml separating funnel, add 0·2 ml of bromothymol blue indicator, 2 ml of sodium citrate solution and then ammonium hydroxide drop by drop until the solution just changes in colour through green to a full blue. Add 30 ml of the buffer solution. The *p*H of the solution will now be 8·7 to 9·3. This solution is then titrated with dithizone.

39.2.4 The titration consists in shaking the solution with controlled additions of dithizone reagent (say 1 ml) together with about 3 ml of chloroform, the lower layer containing the red zinc dithizonate being removed as the titration proceeds. As the end point is approached, the reagent is added in smaller portions and eventually a stage is reached when an addition of 0·1 ml of dithizone reagent and 2 ml of chloroform, and shaking, results in a purplish colour in the solvent layer (as distinct from the pure red of the zinc dithizonate previously obtained). This indicates the presence of a trace of free dithizone and is taken as the end point of the titration. Confirmation of this end point is obtained by removing the solvent layer and shaking the test solution with a further 0·1 ml of dithizone reagent and 2 ml of chloroform, when the extract should remain green or blue. A sharper end point is obtained if towards the end of the titration the red extracts are more completely removed with the aid of 1 to 2 ml of chloroform before the next addition of dithizone reagent is made. Note the total volume of dithizone reagent required for the portion of the *test solution* titrated.

NOTE 1 — All extracts withdrawn during the titration shall be pure red and in the titration of a solution containing much zinc the early extracts shall be removed sufficiently often to obviate any difficulty in detecting the colour due to excess of dithizone in the presence of the strong red colour of the dithizonate.

NOTE 2 — To avoid tedious titrations of unknown amounts of zinc, several devices may usefully be adopted. For example, the solution may be titrated without a very cautious approach to the end point and when excess of dithizone is indicated, an amount of standard zinc solution more than sufficient to react with the excess of dithizone is added. After adequate shaking, the presence of excess of zinc will be clearly indicated by the pure red colour of the chloroform layer and the titration with dithizone is then completed. A correction is applied for the volume of standard zinc solution used. Or, if two or more aliquot portions of the test solution are available, the first portion may be used to get an approximate result and in the titration of further portion, it will be possible to add most of the dithizone in the first extraction and to complete the titration of the remaining zinc with smaller additions of dithizone. If,

however, it is not desirable to use aliquot portions, a part of the test solution may be titrated and the remainder may be held in reserve and added as necessary to the main solution in the separating funnel as indications of excess dithizone are obtained.

39.2.5 Carry out a blank determination on all the reagents used and make the blank solution up to the same volume as the *test solution*. Titrate it with dithizone solution as in **39.2.4**.

39.2.6 *Standardization of Dithizone Reagent* — After titration of the ' blank ' solution (*see* **39.2.5**), draw off the bottom layer and shake the aqueous layer twice with 5-ml portions of chloroform. Reject the chloroform extracts. Add 5 ml of standard zinc solution (that is, 0·05 mg of Zn) and titrate with dithizone reagent. In standardizing, the approximate amount of dithizone reagent required will be known and it is permissible to add the greater part of it at once, together with the appropriate amount of chloroform, the titration being then completed by smaller additions of dithizone reagent. Denote the volume of dithizone reagent required for the 0·05 mg of zinc by x ml. Shake the titrated solution as before with two 5-ml portions of chloroform to remove all traces of excess reagent. Add 25 ml of standard zinc solution (that is, 0·25 mg of Zn) and titrate the solution again. Denote the volume of dithizone reagent required for 0·25 mg of zinc by y ml.

39.3 Calculation

a) $$F = \frac{0{\cdot}2}{y - x}$$

where

F = amount in mg of zinc equivalent to 1 ml of dithizone reagent,

y = volume in ml of dithizone reagent required for titrating 0·25 mg of zinc, and

x = volume in ml of dithizone reagent required for titrating 0·05 mg of zinc.

b) $$\text{Zinc (as Zn), mg/l} = 1\,000\,\frac{F\,(a - b)}{v}$$

where

a = volume in ml of dithizone reagent required for titrating the *test solution*,

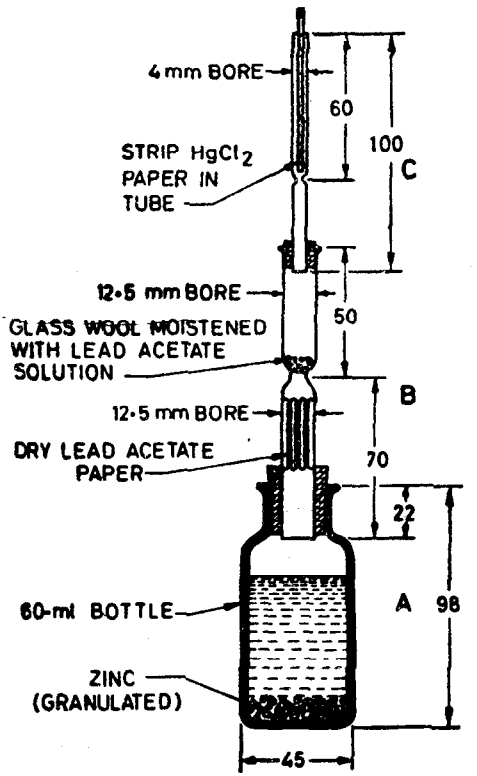
b = volume in ml of dithizone reagent required for titrating the blank, and

v = volume in ml of the sample taken for the test.

40. ARSENIC

40.0 Outline of the Method — The stain produced on mercuric chloride paper is matched against that obtained with a series of standard arsenic solutions.

40.1 Apparatus — The apparatus shall be assembled as shown in Fig. 3.



All dimensions in millimetres.

FIG. 3 APPARATUS FOR DETERMINATION OF ARSENIC

40.2 Reagents

40.2.1 *Concentrated Hydrochloric Acid* — conforming to IS : 265-1962*.

40.2.2 *Lead Acetate Solution* — Prepare one percent solution of lead acetate with sufficient acetic acid added to clear the solution.

40.2.3 *Dry Lead Acetate Paper* — Soak large sheets of qualitative filter paper in lead acetate solution and dry. Cut the paper into pieces measuring 70 × 50 mm.

40.2.4 *Mercuric Chloride Solution* — approximately 0·35 percent *w/v*.

40.2.5 *Sensitized Mercuric Chloride Paper Strips* — Cut 50 × 50 cm filter paper No. 0 into four equal squares and dip them into mercuric chloride solution. The paper should be of uniform thickness otherwise there will be irregularity in the length of the stain for the same amount of arsenic. Hang the squares and dry them in air free from gas fumes, hydrogen sulphide being particularly undesirable. When dry, trim off about 1 cm of the outer edge and cut the paper into strips 12 cm × 2·5 mm. Preserve the strips in bottles with tight-fitting stoppers. Strips with a white deposit of mercuric chloride shall not be used. Stains shall be made with each batch of paper.

40.2.6 *Concentrated Sulphuric Acid* — conforming to IS : 266-1961†.

40.2.7 *Dilute Sulphuric Acid* — approximately 5 N, prepared by diluting concentrated sulphuric acid.

40.2.8 *Stannous Chloride Solution* — Dissolve 80 g of stannous chloride in 100 ml of distilled water containing 5 ml of concentrated hydrochloric acid.

40.2.9 *Zinc* — Treat arsenic-free zinc shots passing 5·60-mm IS Sieve and retained on 2·80-mm IS Sieve, with concentrated hydrochloric acid until the surface of the zinc shots becomes clean and dull. Wash and keep covered with water in a casserole, using a clock-glass to keep out dust.

40.2.10 *Standard Arsenic Trioxide Solution* — Dissolve 1·000 g of resublimed arsenic trioxide (As_2O_3) in 25 ml of sodium hydroxide solution (20 percent *w/v*) and neutralize with dilute sulphuric acid. Dilute with freshly distilled water to which 10 ml of concentrated sulphuric acid per litre has been added and make up the volume to 1 000 ml. Again dilute 10 ml of this solution to 1 litre with water containing sulphuric acid and finally dilute 100 ml of the latter solution to 1 litre with water containing sulphuric acid. One millilitre of the final solution contains 0·001 mg of arsenic trioxide (As_2O_3).

40.3 Procedure

40.3.1 Add 5 ml of concentrated hydrochloric acid to 100 ml of the sample and evaporate down to about 40 ml.

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*Specification for hydrochloric acid (*revised*).

†Specification for sulphuric acid (*revised*).

40.3.2 Place the dry lead acetate paper in the lower portion of the tube *B* and glass wool moistened with lead acetate solution in its upper portion. Place the sensitized strip of mercuric chloride paper in the tube *C* and connect the tubes together with a rubber stopper. Transfer the solution prepared under **40.3.1** into the Gutzeit bottle *A*, and then add 10 ml of dilute sulphuric acid. Add 0·5 ml of stannous chloride solution. Mix the contents and drop about 10 g of zinc shots. Immediately fit in position the rubber stopper carrying the tube *B*. Place the bottle in a warm place at about 40°C. At the end of 45 minutes, remove the test strip by means of tweezers. Carry out the test as prescribed above with different volumes of standard arsenic trioxide solution and compare the stain produced with the sample with those simultaneously obtained from varying amounts of standard arsenic solution.

40.4 Calculation

$$\text{Arsenic (as } As_2O_3\text{), mg/l} = \frac{v}{100}$$

where

v = volume in ml of standard arsenic trioxide solution taken in the control standard which matches the stain produced with the sample.

41. ALKALI METALS

41.0 General — Two methods are prescribed for determination of alkali metals. In the method described in **41.1**, the alkali metals are isolated and determined as their chlorides. In the method described in **41.2**, the alkali metals are calculated from analytical results.

41.1 Alkali Metals by Determination

41.1.0 *Outline of the Method* — After precipitation of other metals with ammonium carbonate and ammonium oxalate, the alkali metals are determined by ignition and weighing.

41.1.1 *Reagents*

41.1.1.1 *Concentrated hydrochloric acid* — conforming to IS : 265-1962*.

41.1.1.2 *Litmus paper*

41.1.1.3 *Barium hydroxide solution* — saturated.

41.1.1.4 *Concentrated ammonium hydroxide* — sp gr 0·92.

41.1.1.5 *Ammonium carbonate solution* — saturated.

41.1.1.6 *Ammonium oxalate solution* — saturated.

*Specification for hydrochloric acid (*revised*).

41.1.2 *Procedure*

41.1.2.1 Evaporate 500 ml of the sample to about 40 ml and transfer to a 100-ml flask. Add concentrated hydrochloric acid until the solution is just acid to litmus paper. Boil gently in the flask to expel carbon dioxide and add barium hydroxide solution drop by drop until the solution is alkaline to litmus and no furhter precipitation is obtained. Cool to room temperature, make up to 100 ml in a volumetric flask, shake well and filter through a filter paper into a beaker, rejecting the first few millilitres of the filtrate. Place 75 ml of the filtrate in a 100-ml conical flask, add a few drops of concentrated ammonium hydroxide and heat to approximately 80°C. Add ammonium carbonate solution until no further precipitation is obtained. Add a few drops of ammonium oxalate solution, cool and make up to 100 ml in a volumetric flask and shake well.

41.1.2.2 Filter through a dry filter paper into a dry beaker, rejecting the first few millilitres of the filtrate. Place 75 ml of the filtrate in a weighed platinum dish and evaporate to dryness. Heat over a small burner until the ammonium salts have been volatilized. Care shall be taken to avoid losses due to decrepitation at the commencement of heating; moreover, the volatilization shall be conducted at the lowest possible temperature in order to avoid losses due to volatilization of alkali chlorides. When the ammonium salts have been expelled, cool the dish, moisten with a few drops of concentrated hydrochloric acid, evaporate to dryness and ignite gently. Cool and weigh as alkali chlorides.

NOTE — The alkali chlorides sometimes contain traces of silica, and a solution of the alkali chlorides in water will show if silica is present. If silica is present, filter off, wash well, ignite and weigh and deduct the weight of the residue from the weight of total alkali chlorides.

41.1.3 *Calculation*

$$\text{Alkali metals (as Na), mg/l} = 1{\cdot}397\ W$$

where

W = weight in mg of alkli chlorides obtained.

41.2 Alkali Metals by Calculation — The alkali metals may be calculated from mineral analysis when the total alkalinity is greater than or equal to total hardness. If total alkalinity is less than total hardness, it is not possible to carry out this calculation.

41.2.1 If total alkalinity (as $CaCO_3$) is greater than total hardness (as $CaCO_3$), then

$$\begin{aligned}\text{Alkali metals (as Na), mg/l} = {} & 0{\cdot}459\,6\ [\ \text{total alkalinity (as } CaCO_3\text{ mg/l)}\ ] \\ & -\ \text{total hardness (as } CaCO_3\text{ mg/l)}\ ] \\ & +\ 0{\cdot}478\,9\ [\ \text{sulphates (as } SO_4\text{ mg/l)}\ ] \\ & +\ 0{\cdot}648\,6\ [\ \text{chlorides (as Cl mg/l)}\ ]\end{aligned}$$

41.2.2 If total alkalinity (as $CaCO_3$) is equal to total hardness (as $CaCO_3$), the alkali metals (as Na) shall be calculated from the amounts of sulphates and chlorides using the factors given in **41.2.1.**

42. TOTAL CARBON DIOXIDE

42.0 Outline of the Method — Carbon dioxide is liberated by acidifying and heating the sample in a closed system. The carbon dioxide is absorbed in an alkaline barium chloride solution and the barium carbonate formed is determined by titration.

42.1 Apparatus

42.1.1 *Distillation Apparatus* — assembled as shown in Fig. 4.

42.1.2 *Apparatus for Storing Barium Chloride Solution* — assembled as shown in Fig. 5.

42.2 Reagents

42.2.1 *Dilute Hydrochloric Acid* — 1 : 3 *v/v.*

42.2.2 *Phenolphthalein Indicator Solution* — same as in **14.1.1.**

42.2.3 *Barium Chloride Solution* — about 0·5 M.

42.2.4 *Methyl Orange Indicator Solution* — same as in **13.1.2.**

42.2.5 *Standard Sodium Hydroxide Solution* — 1 N and 0·1 N, standardized with methyl orange as indicator.

42.2.6 *Standard Hydrochloric Acid* — 1 N and 0·1 N.

42.3 Procedure

42.3.1 Into the 500-ml Kjeldahl flask *D* of the distillation apparatus, add 50 ml of dilute hydrochloric acid. Into flask *E*, add 50 ml of distilled water and a few drops of phenolphthalein indicator solution and connect *B*, *D* and *E* as shown in Fig. 4 with the rubber cap *G* but without the soda-lime tower *A*. Close tap *C* and evacuate by a water pump through tap *F* until the pressure is below 3 cm of mercury. Close tap *F*.

42.3.2 In the aspirator *J* of the apparatus for storing barium chloride solution (*see* Fig. 5), add a mixture of equal volumes of barium chloride solution and standard sodium hydroxide solution (1 *N*). In the aspirator *H*, take distilled water. From aspirator *J*, run the liquid into a 45-ml bulb burette *K*, with the tap *L* shut, until the burette reads 0 ml. The volume of this solution to be used, which is approximately 0·5 N, should be equivalent to an excess of 10 ml of 0·5 N over the total alkalinity contained in the volume of the sample taken for the test. Connect the tap *F* in Fig. 4

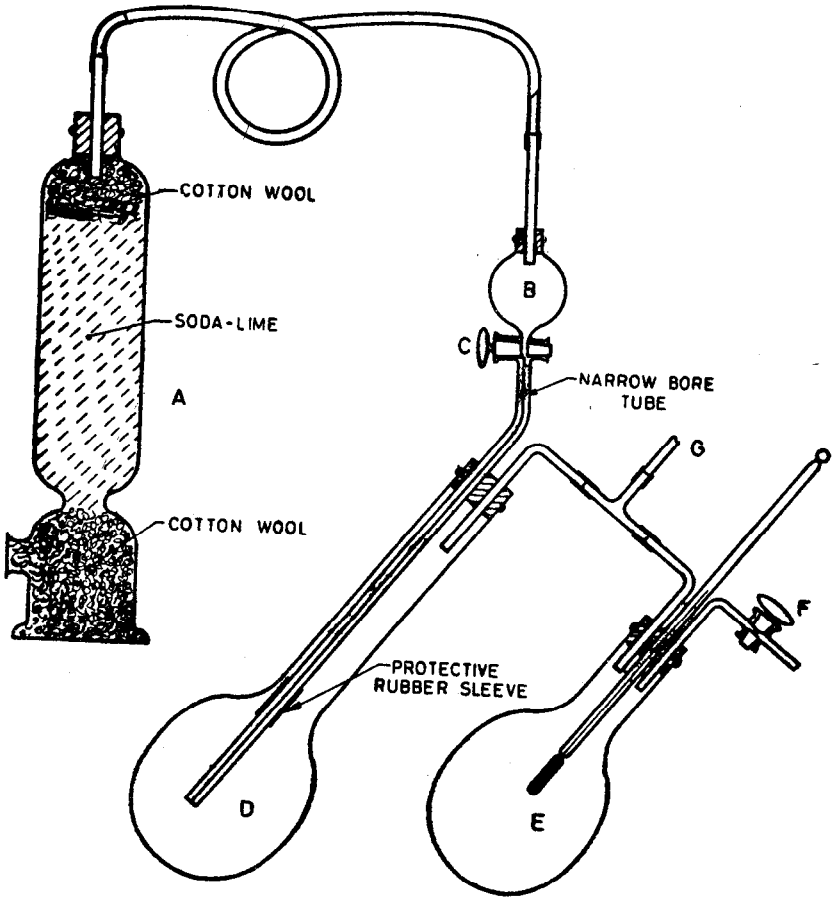

FIG. 4 DISTILLATION APPARATUS

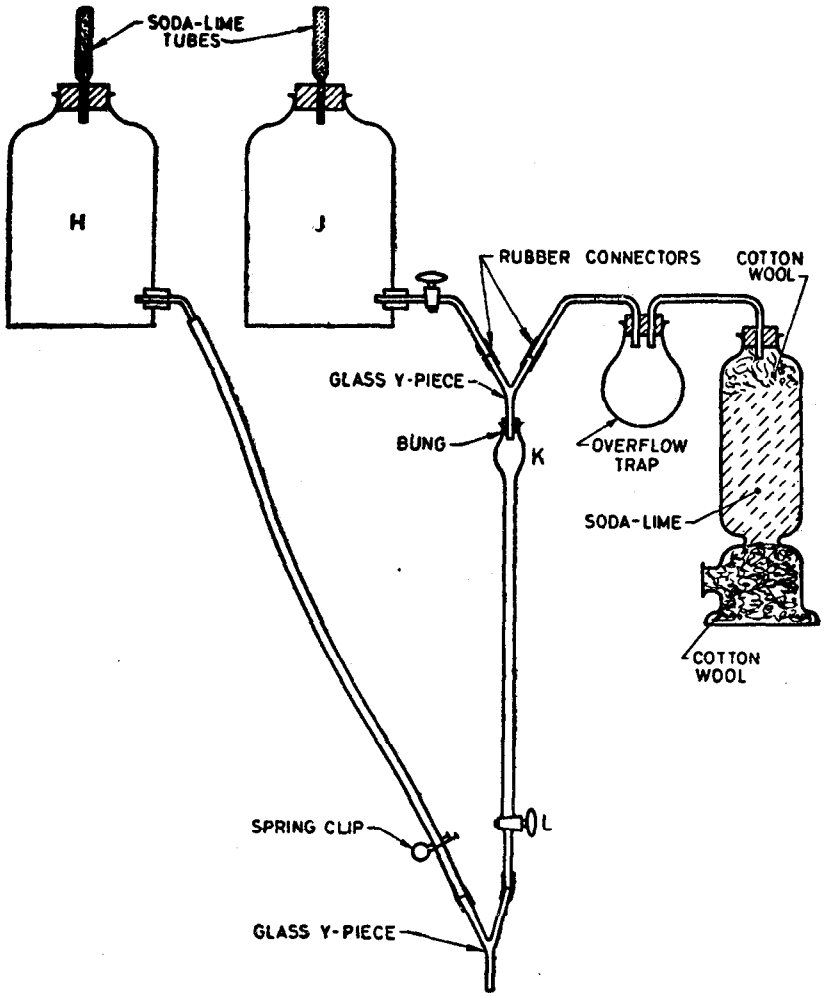

FIG. 5 APPARATUS FOR STORING BARIUM CHLORIDE SOLUTION

to the bottom limb of the Y-piece below tap *L* in Fig. 5 by means of a short length of rubber tubing, open taps *F* and *L* and allow the required volume of liquid to run from the burette. Shut tap *L*. Open the spring clip to allow distilled water from the aspirator *H* to flush out the connections and run into flask *E*. Close the spring clip and tap *F*. Disconnect the rubber tubing from the bottom limb of the Y-piece. Connect tap *F*, while still shut, to a water pump running at full bore, open tap *F* and re-evacuate. Close tap *F*. Disconnect the water pump.

42.3.3 Into the funnel *B*, run 200 ml of the sample. Connect tower *A* to *B*. Open tap *C*. Run most of the sample from *B* into flask *D*. Close tap *C*, leaving about 0·5 ml of the sample in *B*. Disconnect the tower *A* from *B*. Run 5 ml of freshly boiled and cooled distilled water into *B*. Connect the tower *A* to *B* and open tap *C*. Run most of the solution from *B* into flask *D*, then close tap *C*, leaving about 0·5 ml of the solution in *B*. Repeat this rinsing of *B* in the same manner once more using 5 ml of freshly boiled and cooled distilled water. A small volume of the liquid should be left in *B* to prevent possible ingress of air. Heat flask *D* with a Bunsen flame and shake the apparatus. This is simplified by having a felt pad below the retort stand. Continue heating until the thermometer in *E* reads 70°C. Remove the flame. Open tap *C* to allow air free from carbon dioxide to enter the apparauts. Let the apparatus cool.

42.3.4 Remove flask *E* and add a few drops of phenolphthalein indicator solution. Run standard hydrochloric acid (1 N) carefully into *E* until the phenolphthalein colour is nearly discharged. Complete the titration to the phenolphthalein end point using standard hydrochloric acid (0·1 N). To the contents of the flask, add standard hydrochloric acid (1 N or 0·1 N), according to the amount of carbonate present, with shaking until the precipitate dissolves. Add 2 ml in excess and note the reading. Add 2 drops of methyl orange indicator and titrate the excess acid with standard sodium hydroxide solution (1 N or 0·1 N) corresponding to the strength of acid previously used. Record as millilitres of 1 N acid and alkali respectively.

42.3.5 Carry out a blank determination on the reagents used. Subtract the number of millilitres of 1 N sodium hydroxide required for the last titration from the millilitres of 1 N hydrochloric acid used to dissolve the barium carbonate, to obtain the number of millilitres of a normal solution equivalent to the carbon dioxide present. Let this figure be *X* and the corresponding blank be *Y*.

42.4 Calculation

$$\text{Total carbon dioxide (as } CO_2\text{), mg/l} = \frac{22\,000\,(X - Y)}{V}$$

where

X = volume in ml of 1 N hydrochloric acid added in **42.3.4**, minus the volume in ml of 1 N sodium hydroxide solution used in **42.3.4**,

Y = volume in ml of 1 N hydrochloric acid minus the volume in ml of 1 N sodium hydroxide solution used in the blank determination, and

V = volume in ml of the sample taken for the test.

43. FREE CARBON DIOXIDE

43.0 General

43.0.1 *Outline of the Method* — The sample is titrated with standard sodium carbonate solution or standard barium hydroxide solution, using phenolphthalein indicator.

43.0.2 Two methods are prescribed for the determination of free carbon dioxide. Method *A* is applicable in the range 5 to 50 mg/l in terms of calcium carbonate and Method *B* is applicable up to 5 mg/l in terms of calcium carbonate.

43.1 Method A

43.1.1 *Reagents*

43.1.1.1 *Phenolphthalein indicator solution* — same as in **14.1.1.**

43.1.1.2 *Standard sodium carbonate solution* — 0·02 N.

43.1.1.3 *Buffer solution* — Dissolve 1·237 g of boric acid in carbon dioxide-free distilled water and make up to 100 ml (solution *A*). Dissolve 1·491 g of potassium chloride in carbon dioxide-free distilled water and make up to 100 ml (solution *B*). Mix 25 ml of solution *A* with 25 ml of solution *B*, add to the mixture 2·95 ml of an exactly 0·2 N sodium hydroxide solution and dilute with carbon dioxide-free distilled water to 100 ml. When required for use, dilute 10 ml of the solution to 100 ml with carbon dioxide-free distilled water.

43.1.2 *Procedure* — Pipette out 200 ml of the sample into a 250-ml glass-stoppered bottle. Add 1 ml of phenolphthalein indicator solution and titrate in the bottle with standard sodium carbonate solution, using only gentle agitation. Compare the tint with that obtained with 100 ml of buffer solution contained in a similar bottle to which 1 ml of indicator solution has been added. At the end point, the tint of the sample and the control shall be identical after one minute. The stopper shall be replaced after each addition of sodium carbonate solution.

43.1.3 *Calculation*

a) Free carbon dioxide (as CO_2), mg/l = $2·2\ V$

b) Free carbon dioxide (as $CaCO_3$), mg/l = $5\ V$

where

V = volume in ml of standard sodium carbonate solution used in the titration.

43.2 Method B

43.2.1 *Apparatus*

43.2.1.1 *Sampling flask* — A 500-ml conical flask fitted with a rubber bung through which pass two glass tubes, the inlet tube reaching to the bottom of the flask and the outlet tube ending nearly flush with the bottom of the rubber bung. To each tube is connected a length of soft rubber tubing fitted with a spring clip.

43.2.1.2 *Guard tube* — containing soda-lime for fitting to the outlet of the sampling flask.

43.2.1.3 *Semi-micro burette* — capacity 1 ml. This is fitted with a fine immersion jet formed either by drawing out a length of glass tubing and connecting it to the tip of the burette with thick-walled rubber tubing, or by drawing out the tip of the burette.

43.2.2 *Reagents*

43.2.2.1 *Nitrogen* — pure. If nitrogen supply is not available, air free from carbon dioxide may be used.

43.2.2.2 *Phenolphthalein indicator solution* — same as in **14.1.1.**

43.2.2.3 *Standard barium hydroxide solution* — 0·01 N.

43.2.3 *Procedure* — Collect the sample in the sampling flask, taking care to remove all bubbles and allowing about ten replacements of the sample to flow through the flask. Close the sample valve, then the clips. Wash a second 500-ml conical flask with distilled water and pass nitrogen through a bent glass tube hooked over the side of the flask and reaching nearly to the bottom. Fit the guard tube to the outlet of the sampling flask, hold the inlet tube so that it will act as a siphon, open both clips and allow about 100 ml of the sample to flow into the titration flask, taking care not to bubble nitrogen through the sample. Add 0·2 ml of phenolphthalein indicator solution and titrate with standard barium hydroxide solution, swirling gently during the titration and maintaining the flow of nitrogen above the sample. Note the reading of the burette when a distinct rose or pink colour develops. Pour the titrated sample into a measuring cylinder and note the volume.

43.2.4 *Calculation*

a) Free carbon dioxide (as CO_2), mg/l $= 440 \frac{V_1}{V_2}$

b) Free carbon dioxide (as $CaCO_3$), mg/l $= 1\,000 \frac{V_1}{V_2}$

where

V_1 = volume in ml of standard barium hydroxide solution used in the titration, and

V_2 = volume in ml of the sample taken for the titration.

44. CARBONATES AND BICARBONATES

44.0 Outline of the Method — The sample is titrated with standard acid, using first phenolphthalein and then methyl orange indicator.

44.1 Reagents

44.1.1 *Phenolphthalein Indicator Solution* — same as in **14.1.1.**

44.1.2 *Standard Sulphuric Acid* — 0·05 N.

44.1.3 *Methyl Orange Indicator Solution* — same as in **13.1.2.**

44.2 Procedure — Take 100 ml of the sample and add a few drops of phenolphthalein indicator solution. If pink colour is produced, titrate with standard sulphuric acid, adding a drop every two to three seconds until the colour disappears. Note the volume of acid added. To the colourless solution obtained in the above titration, or if no pink colour is produced with phenolphthalein, to the original solution, add 1 to 2 drops of methyl orange indicator solution and titrate with standard sulphuric acid to the end point and note the total volume of acid added (including that added in titration with phenolphthalein).

44.3 Calculation

a) Carbonates (as CO_3), mg/l $= 30\ v_1$

b) Bicarbonates (as HCO_3), mg/l
(in absence of carbonates) $= 30{\cdot}5\ v_2$

c) Bicarbonates (as HCO_3), mg/l
(in presence of carbonates) $= 30{\cdot}5\ (v_2 - 2v_1)$

where

v_1 = volume in ml of standard sulphuric acid added in titration with phenolphthalein indicator, and

v_2 = total volume in ml of standard sulphuric acid added in titration with phenolphthalein and methyl orange indicators.

45. RESIDUAL CHLORINE

45.0 General

45.0.1 *Outline of the Method* — Residual chlorine reacts under acid conditions with *o*-tolidine to give a yellow colour which is matched against standard colours.

45.0.2 Residual chlorine determination should be carried out at a temperature between 15 and 20°C, and during the colour development the

treated solutions should be kept in the dark or in subdued light. With the method prescribed, it is possible to distinguish between ' free residual chlorine ' and ' combined residual chlorine '.

45.1 Apparatus

45.1.1 *Nessler Cylinders* — 100 ml capacity.

45.2 Reagents

45.2.1 *o-Tolidine Reagent* — Weigh out 1 g of *o*-tolidine (melting point 129°C), transfer to a 15-cm mortar and add 5 ml of dilute hydrochloric acid (1 : 4 *v/v*). Grind to a thin paste and add 150 to 200 ml of distilled water. Transfer the solution to a 1-litre graduated cylinder and make up to 500 ml with water. Make up to 1 litre by the addition of dilute hydrochloric acid. Store in an amber coloured glass-stoppered bottle and keep in the dark.

45.2.2 *Sodium Arsenite Solution* — Dissolve 0·5 g of sodium meta-arsenite in distilled water and make up to 100 ml.

45.2.3 *Copper Sulphate Solution* — Dissolve 1·5 g of copper sulphate ($CuSO_4.5H_2O$) in 50 to 60 ml of distilled water, add 1 ml of concentrated sulphuric acid (conforming to IS : 266-1961*) and make up to 100 ml.

45.2.4 *Potassium Dichromate Solution* — Dissolve 0·25 g of potassium dichromate in distilled water, add 1 ml of concentrated sulphuric acid (conforming to IS : 266-1961*) and make up to 1 litre.

45.2.5 *Standard Colour Solutions* — Measure into 100-ml Nessler cylinders the volumes of copper sulphate solution and potassium dichromate solution given in Table 4 and dilute to 100 ml with distilled water. In col 2 of the table are given the amounts of chlorine to which the colour solutions are equivalent.

45.3 Procedure — Use three Nessler cylinders and designate them as cylinders *A*, *B* and *C*. In cylinder *A*, add 1·0 ml of *o*-tolidine reagent, 100 ml of the sample, mix and add immediately 2 ml of sodium arsenite solution. Mix and after two minutes match the colour with the standard colour solutions. This reading (*FR*) represents the total of free residual chlorine and any interfering substances. In cylinder *B*, add 2 ml of sodium arsenite solution and 100 ml of the sample, mix and add immediately 1·0 ml of *o*-tolidine reagent. Mix and after two minutes match the colour with standard solutions. This reading (B_1) is the blank for interfering substances after two minutes standing. Retain the solution and after 15 minutes again match the colour. This reading (B_2) is the blank for interfering substances after 15 minutes standing. In cylinder *C*, add 1·0 ml of *o*-tolidine

*Specification for sulphuric acid (*revised*).

reagent and 100 ml of the sample, mix and after 15 minutes match the colour. This reading (TR) gives the total residual chlorine plus interfering substances.

TABLE 4 STANDARD COLOUR SOLUTIONS FOR RESIDUAL CHLORINE DETERMINATION

(*Clause* 45.2.5)

Sl No.	Chlorine	Copper Sulphate Solution	Potassium Dichromate Solution
(1)	(2)	(3)	(4)
	mg/l	ml	ml
i)	0·01	0	0·8
ii)	0·02	0	2·1
iii)	0·03	0	3·2
iv)	0·04	0	4·3
v)	0·05	0·4	5·5
vi)	0·06	0·8	6·6
vii)	0·07	1·2	7·5
viii)	0·08	1·5	8·2
ix)	0·09	1·7	9·0
x)	0·10	1·8	10·0
xi)	0·15	1·8	15·0
xii)	0·20	1·9	20·0
xiii)	0·25	1·9	25·0
xiv)	0·30	1·9	30·0
xv)	0·35	1·9	34·0
xvi)	0·40	2·0	38·0
xvii)	0·50	2·0	45·0
xviii)	0·60	2·0	51·0
xix)	0·70	2·0	58·0
xx)	0·80	2·0	63·0
xxi)	0·90	2·0	67·0
xxii)	1·00	3·0	72·0

45.4 Calculation

a) Free residual chlorine (as Cl), mg/l = $FR - B_1$

b) Total residual chlorine (as Cl), mg/l = $TR - B_2$

c) Combined residual chlorine (as Cl), mg/l = $(TR - B_2) - (FR - B_1)$

45.5 Range — The method is applicable up to 5 mg/l of chlorine.

46. SULPHIDES

46.0 Outline of the Method — The sulphides are precipitated as cadmium sulphide which is then treated with an acid. The hydrogen sulphide evolved is absorbed in a measured volume of standard iodine solution.

46.1 Apparatus — An all-glass distillation apparatus as shown in Fig. 6 shall be assembled.

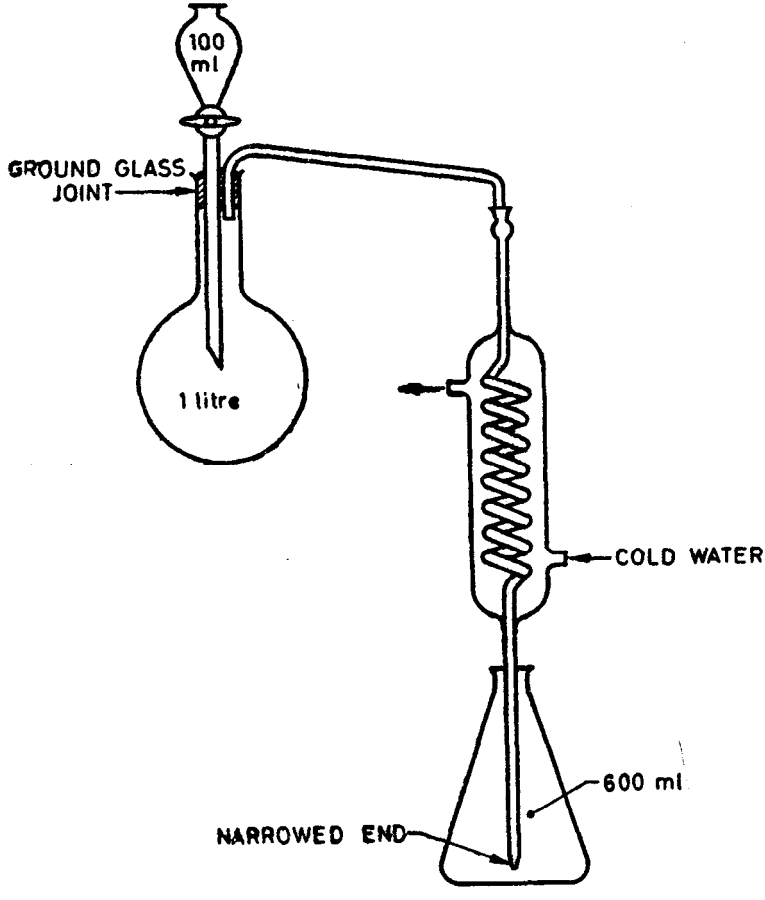

FIG. 6 APPARATUS FOR SULPHIDE DETERMINATION

46.2 Reagents

46.2.1 *Cadmium Sulphate Solution* — 20 percent *w/v*.

46.2.2 *Dilute Sulphuric Acid* — 1 : 1 *v/v*.

46.2.3 *Standard Iodine Solution* — 0·1 N.

46.2.4 *Standard Sodium Thiosulphate Solution* — 0·1 N, freshly standardized.

46.2.5 *Starch Indicator* — same as in **21.1.2**.

46.3 Procedure

46.3.1 To a volume of the sample varying between 500 ml and 2 000 ml according to the amount of hydrogen sulphide expected, add immediately after collection 20 ml of cadmium sulphate solution and mix. A yellow precipitate of cadmium sulphide is formed if hydrogen sulphide is present. This procedure immediately fixes any hydrogen sulphide, thus preventing oxidation.

46.3.2 Filter the sample through a 11-cm medium ashless filter paper and remove any trace of precipitate from the sample bottle with a little filter paper pulp and a few millilitres of distilled water. It may be more convenient to filter the precipitate of cadmium sulphide on the site, then pack the filter paper and precipitate in a suitable bottle and send to the laboratory. The filtration may be done either through a filter paper of medium texture or through a filter funnel containing a pad of filter paper pulp. In the latter case, connect the funnel to a Buchner flask through a rubber stopper and apply suction by means of a vacuum pump.

46.3.3 Place the filter paper containing the precipitate in the flask of the distillation apparatus and then add 500 ml of distilled water which has been previously boiled and cooled. Heat the mixture to boiling and while boiling, add slowly 100 ml of dilute sulphuric acid through the tap funnel. Collect the hydrogen sulphide which is liberated in 30 ml of standard iodine solution. Continue the distillation until the yellow cadmium sulphide has disappeared, then for a further 10 minutes. Titrate the excess iodine with standard sodium thiosulphate solution using starch solution as indicator. Carry out a blank determination on reagents used by the method described above, commencing at the point where 100 ml of dilute sulphuric acid are added to 500 ml of distilled water.

46.4 Calculation

$$\text{Sulphides (as } H_2S\text{), mg/l} = 17\,000\,\frac{(V_1 - V_2)\,N}{V_3}$$

where

V_1 = volume in ml of standard sodium thiosulphate solution used in the blank titration,

V_2 = volume in ml of standard sodium thiosulphate solution used in the test with the sample,

N = normality of standard sodium thiosulphate solution, and

V_3 = volume in ml of the sample taken for the test.

46.5 Range — This method is applicable within the range 1 to 30 mg of sulphides (as H_2S).

47. AMMONIACAL AND ALBUMINOID NITROGEN

47.0 General

47.0.1 *Outline of the Method* — For ammoniacal nitrogen the sample is buffered and distilled. The ammonia in the distillate is treated with Nessler reagent and the colour obtained is matched against that produced with a series of standard ammonium chloride solutions. After removal of free ammonia, albuminoid ammonia is liberated by distilling with alkaline permanganate solution.

47.0.2 If the sample cannot be tested on the day of collection, a special sample for this determination shall be taken and the ammonia fixed by the addition of concentrated sulphuric acid in the proportion of 1 ml/litre of the sample. The determination shall be carried out in an atmosphere free from ammonia.

47.1 Apparatus

47.1.1 *Distillation Flask* — capacity 1 litre and having ground-glass joints.

47.1.2 *Nessler Tubes* — 50 ml capacity.

47.2 Reagents

47.2.1 *Ammonia-Free Water* — This shall be prepared by re-distillation of water after the addition of a few drops of dilute sulphuric acid. The first runnings shall be tested for freedom from ammonia and rejected if necessary.

47.2.2 *Phosphate Buffer Solution* — Dissolve 14·3 g of potassium dihydrogen phosphate (KH_2PO_4) and 90·2 g of dipotassium hydrogen phosphate (K_2HPO_4) in ammonia-free water and make up to 1 litre.

47.2.3 *Nessler Reagent* — Dissolve 35 g of potassium iodide in 100 ml of distilled water. Add to it a cold saturated solution of mercuric chloride until, after thorough mixing, a slight red precipitate remains. Now add

120 g of sodium hydroxide and when dissolved, dilute to 1 litre. Finally add a little more of mercuric chloride solution to produce red colour. Set aside to clear. The reagent shall be shaken occasionally.

47.2.4 *Standard Ammonium Chloride Solution* — Dissolve 3·82 g of ammonium chloride, dried at 100°C, in ammonia-free water and make up to 1 litre with ammonia-free water. Dilute 10 ml of the solution with ammonia-free water to 1 000 ml when required for use. One millilitre of the diluted solution is equivalent to 0·01 mg of nitrogen (as N).

47.2.5 *Alkaline Potassium Permanganate Solution* — Dissolve 8 g of potassium permanganate in distilled water, add 200 g of sodium hydroxide, dissolve and make up to 1 litre. Before using the solution, add an equal volume of distilled water and then boil until the solution is restored to its original volume.

47.3 Procedure

47.3.1 *For Ammoniacal Nitrogen* — Ensure that the distillation apparatus is free from ammonia by distilling a little ammonia-free water in it until the distillate shows a negative test for ammonia. Empty the flask and add 500 ml of the sample (*see* Note 2) followed by 10 ml of phosphate buffer solution. Collect the first 300 ml of distillate (*see* Note 3) and make up the volume of the distillate to 500 ml with ammonia-free water. Take a 50-ml aliquot, add 2 ml of Nessler reagent and mix well. Match the colour after 5 minutes with that produced by suitable quantities (0·3 to 3 ml) of standard ammonium chloride solution. Express the result to the nearest 0·01 mg/l. Keep the distillation flask with its contents for test in **47.3.2.**

NOTE 1 — If the sample contains residual chlorine, dechlorinate with a trace of sodium sulphite before commencing distillation.

NOTE 2 — If the content of albuminoid nitrogen in the sample is greater than about 0·3 mg/l, take only 250 ml of the sample instead of 500 ml and make up to 500 ml with ammonia free water.

NOTE 3 — If the content of ammoniacal nitrogen is expected to be high, collect the first 100 ml of the distillate and take an aliquot for the determination. Collect subsequent 50-ml portions of the distillate until free of ammonia and determine the total ammoniacal nitrogen content of all such portions of the distillate by the method given in **47.3.1.**

47.3.2 *For Albuminoid Nitrogen* — Dilute the contents of the distillation flask (*see* **47.3.1**) to 300 ml with ammonia-free water and add 50 ml of alkaline potassium permanganate solution to it. Distil at a rate not less than 6 ml nor more than 10 ml per minute. Collect the first 200 ml of the distillate (*see* Note) and dilute to 250 ml with ammonia-free water. Determine the ammonia content in a 50-ml aliquot following the procedure given in **47.3.1.** Express the result to the nearest 0·01 mg/l.

NOTE — If the content of albuminoid nitrogen in the sample is high, collect the first 100 ml of the distillate and take an aliquot for the determination. Collect subsequent 50-ml portions of the distillate until free of ammonia and determine the total albuminoid nitrogen content of all such portions of the distillate by the method given in **47.3.2.**

47.4 Calculation

47.4.1 *For Ammoniacal Nitrogen*

$$\text{Ammoniacal nitrogen (as N), mg/l} = 100 \frac{V_1}{V_2}$$

where

V_1 = volume in ml of standard ammonium chloride solution required to match the colour in **47.3.1**, and

V_2 = volume in ml of the sample taken for the test in **47.3.1.**

47.4.2 *For Albuminoid Nitrogen*

$$\text{Albuminoid nitrogen (as N), mg/l} = 50 \frac{V_3}{V_2}$$

where

V_3 = volume in ml of standard ammonium chloride solution required to match the colour in **47.3.2**, and

V_2 = volume in ml of the sample taken for the test in **47.3.1.**

47.5 Range — The method is applicable up to the range 25 μg of nitrogen (as N).

48. NITRATE NITROGEN

48.0 General — Two methods are prescribed. The reduction method given in **48.1** is the referee method and shall be used in case of a dispute. The salicylate method given in **48.2** shall be the alternate method.

48.1 Reduction Method

48.1.0 *Outline of the Method* — The nitrates in the sample are reduced to ammonia which gives a brown colour with Nessler reagent. The colour obtained is matched against that produced with a series of standard ammonium chloride solutions.

48.1.1 *Apparatus*

48.1.1.1 *Nessler tubes* — 50 ml capacity.

48.1.2 *Reagents*

48.1.2.1 *Ammonia-free water* — same as in **47.2.1.**

48.1.2.2 *Sodium hydroxide solution* — Dissolve 250 g of sodium hydroxide in 1 250 ml of ammonia-free water. Add 2 or 3 strips of aluminium foil and allow to stand for 12 hours. Concentrate the solution to 1 litre by boiling.

48.1.2.3 *Aluminium foils* — Strips of aluminium sheet, weighing about 0·5 g each.

48.1.2.4 *Nessler reagent* — same as in **47.2.3.**

48.1.2.5 *Standard ammonium chloride solution* — same as in **47.2.4.**

48.1.3 *Procedure* — Take 100 ml of the sample, or a quantity containing 0·1 mg or less of nitrogen, in a dish, add 2 ml of sodium hydroxide solution and concentrate by boiling to about one third of the original volume. Transfer quantitatively to a 100-ml test tube and dilute to about 75 ml. Prepare a blank (preferably several blanks, since nitrogen impurity in aluminium is often distributed unevenly) by placing about 75 ml of ammonia-free water and 2 ml of sodium hydroxide solution in 100-ml test tube. Place a strip of aluminium foil in each tube. Close the mouth of the test tubes with rubber stoppers connected by means of bent glass tubes with other test tubes containing about 50 ml of slightly acidified ammonia-free water. (These latter tubes serve as traps to prevent escape of ammonia and at the same time permit free evolution of hydrogen.) Allow the sample and the blank to stand at room temperature for 12 hours or until reduction is complete. Nesslerize the traps. If high in ammonia, indicating frothing over of sample, discard the determination. Disregard traps if they contain only 0·01 to 0·02 mg each of the nitrogen (as NH_3). Transfer the sample and blank to distillation flasks, using 250 ml of ammonia-free water for each. Distil at the rate of about one tubeful in 10 minutes into 50-ml Nessler tubes until ammonia ceases to be evolved (4 or 5 tubes are usually sufficient). Add to each tube 2 ml of the Nessler reagent and allow to stand for 10 minutes. From a small burette, measure into another series of Nessler tubes definite quantities of standard ammonium chloride solution, dilute contents of each tube to 50 ml with ammonia-free water, add 2 ml of the Nessler reagent and match the intensity of colour with that obtained in the various Nessler tubes containing the distillate.

48.1.3.1 Nitrites are reduced along with nitrates. A correction shall be applied for their interference.

48.1.4 *Calculation* — Calculate as below and report to the nearest 0·1 mg/l:

$$\text{Nitrate nitrogen (as N), mg/l} = 10 \frac{V_1}{V_2}$$

where

V_1 = total volume in ml of standard ammonium chloride solution required to match the colour obtained in the various Nessler tubes containing the distillate, and

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

48.1.5 *Precision and Accuracy* — The limitations of the reduction method make it difficult to define the precision and accuracy. With some samples,

precision and accuracy of the order of 0·05 mg/l in the range up to 1 mg/l are attained while with other samples much greater errors have been demonstrated.

48.2 Salicylate Method

48.2.0 *Outline of the Method* — The sample is treated with sodium salicylate in the presence of sulphuric acid; the mixture is then made alkaline and the colour obtained is matched against that produced with a series of standard nitrate solutions.

48.2.1 *Apparatus*

48.2.1.1 *Nessler tubes* — 50 ml capacity.

48.2.2 *Reagents*

48.2.2.1 *Sodium chloride solution* — 2 percent *w/v*.

48.2.2.2 *Sodium salicylate solution* — Dissolve 5 g of sodium salicylate in 50 ml of sodium hydroxide solution (1 N) and dilute with distilled water to 1 litre.

48.2.2.3 *Concentrated sulphuric acid* — conforming to IS : 266-1961*.

48.2.2.4 *Sodium hydroxide solution* — approximately 4 N.

48.2.2.5 *Standard nitrate solution* — Dissolve 0·144 g of potassium nitrate in a graduated flask and dilute to 1 litre. Dilute 50 ml of this solution again to 500 ml. One millilitre of the diluted solution is equivalent to 0·002 mg of nitrogen (as N).

48.2.3 *Procedure* — Adjust the volume of the sample by evaporation or dilution so that 25 ml shall contain not more than 0·02 mg of nitrates (as N). Transfer the sample to a porcelain dish. Add five drops of sodium chloride solution and 1 ml of sodium salicylate solution and evaporate to dryness on a water-bath. Moisten the residue, after cooling, with 1 ml of concentrated sulphuric acid and allow to react for exactly 10 minutes. Transfer the contents of the dish quantitatively to a Nessler tube and add 10 ml of sodium hydroxide solution. Make up to the mark with distilled water. Compare the colour obtained with a series of Nessler tubes containing varying amounts of standard nitrate solution treated similarly.

48.2.4 *Calculation*

$$\text{Nitrate nitrogen (as N), mg/l } 000 = \frac{W}{V}$$

where

W = amount in mg of nitrates (as N) present in the Nessler tube with which a match is obtained, and

V = volume in ml of the sample taken for the test.

*Specification for sulphuric acid (*revised*).

49. NITRITE NITROGEN

49.0 Outline of the Method — The nitrite in the sample is acidified and the nitrous acid formed diazotises sulphanilic acid; the latter couples with an amine to give a reddish purple colour which is matched against that produced with a series of standard nitrite solutions.

49.1 Apparatus

49.1.1 *Nessler Tubes* — 50 ml capacity.

49.2 Reagents

49.2.1 *Aluminium Hydroxide Suspension* — Dissolve 125 g of potassium or ammonium alum in 1 litre of distilled water. Warm to 60°C and add slowly, with stirring, 55 ml of concentrated ammonium hydroxide. After it has stood for about one hour, transfer the mixture to a large bottle and wash the precipitate thoroughly by successive decantations with distilled water until free from ammonia, chloride, nitrite and nitrate.

49.2.2 *Sulphanilic Acid Reagent* — Completely dissolve 0·60 g of sulphanilic acid in 70 ml of hot distilled water; cool the solution and add 20 ml of concentrated hydrochloric acid. Dilute to 100 ml with distilled water and mix thoroughly.

49.2.3 *1-Naphthylamine Hydrochloride Reagent* — Dissolve 0·60 g of 1-naphthylamine hydrochloride in distilled water to which 1·0 ml of concentrated hydrochloric acid has been added. Dilute to 100 ml with distilled water and mix thoroughly. The reagent becomes discoloured and a precipitate may form after one week, but it is still usable. It should be discarded when the sensitivity or reproducibility is affected. Storage in a refrigerator extends the life of the reagent. Filter before using.

49.2.4 *Sodium Acetate Buffer Solution* — Dissolve 16·4 g of anhydrous sodium acetate in distilled water and dilute to 100 ml. Filter if necessary.

49.2.5 *Stock Nitrite Solution* — Dissolve 0·246 g of anhydrous sodium nitrite in nitrite-free distilled water and dilute to 1 litre. Preserve by adding 1 ml of chloroform. One millilitre of this solution contains 0·05 mg of nitrite nitrogen (as N).

49.2.6 *Standard Nitrite Solution* — Dilute 10·0 ml of stock nitrite solution to 1 litre with nitrite-free distilled water. Preserve by adding 1 ml of chloroform and store in a sterilized bottle. One millilitre of this solution contains 0·000 5 mg of nitrite nitrogen (as N).

49.3 Procedure

49.3.1 If the sample contains suspended solids and colour, add 2 ml of aluminium hydroxide suspension to 100 ml of sample; stir thoroughly,

allow to stand for a few minutes, and filter, discarding the first portion of the filtrate.

49.3.2 To 50 ml of clear sample which has been neutralized to a *p*H of 7, or to an aliquot diluted to 50 ml, add 1·0 ml of sulphanilic acid reagent and mix thoroughly. At this point, the *p*H of the solution should be about 1·4. After 10 minutes, add 1·0 ml of 1-naphthylamine hydrochloride reagent and 1·0 ml of sodium acetate buffer solution, and mix well. At this point, the *p*H of the solution should be 2·0 to 2·5. After 10 to 30 minutes, compare visually the reddish-purple colour with that of the standards prepared with varying quantities of standard nitrite solution treated similarly.

49.4 Calculation

$$\text{Nitrite nitrogen (as N), mg/l} = 1\,000\,\frac{W}{V}$$

where

W = amount in mg of nitrite nitrogen (as N) contained in the standard matching the colour obtained with the sample, and

V = volume in ml of the sample taken for the test.

49.5 Precision and Accuracy — On undiluted samples and in the absence of interference, the precision and accuracy are estimated to be within 0·002 mg/l in the range up to 0·025 mg/l (as N).

50. DISSOLVED OXYGEN

50.0 Outline of the Method — The dissolved oxygen in the sample oxidizes manganous hydroxide to manganic hydroxide which, in turn, oxidizes iodide to free iodine in an acid medium. The iodine liberated is determined by titation.

50.1 Interference — The method given here is most suitable for waters containing not more than 0·1 mg/l of nitrite nitrogen and not more than 1 mg/l of ferrous iron. Other reducing or oxidizing materials should be absent. If 1 ml of potassium fluoride solution is added before acidifying the sample and there is little delay in titrating, the method is also applicable in the presence of 100 to 200 mg/l of ferric iron.

50.2 Reagents

50.2.1 *Manganous Sulphate Solution* — Dissolve 480 g of manganous sulphate ($MnSO_4.4H_2O$) in distilled water, filter and dilute to 1 litre. The solution should liberate not more than a trace of iodine when added to an acidified solution of potassium iodide.

50.2.2 *Iodide-Azide Reagent* — Dissolve 500 g of sodium hydroxide (or 700 g of potassium hydroxide) and 135 g of sodium iodide (or 150 g of potassium iodide) in distilled water and dilute to 1 litre. The reagent should not give a colour with starch solution when diluted and acidified. Dissolve 10 g of sodium azide in 40 ml of distilled water and add to 950 ml of the first solution, with constant stirring.

50.2.3 *Concentrated Sulphuric Acid* — approximately 36 N. One millilitre of the acid is equivalent to about 3 ml of iodide-azide reagent.

50.2.4 *Standard Sodium Thiosulphate Solution* — exactly 0·025 N, freshly standardized against potassium dichromate. One millilitre of this solution is equivalent to 0·2 mg of oxygen (as O).

50.2.5 *Starch Indicator Solution* — same as in **21.1.2.**

50.3 Procedure — To the sample as collected in a 250 to 300 ml bottle, add 2 ml of manganous sulphate solution, followed by 2 ml of iodide-azide reagent well below the surface of the liquid. Stopper with care to exclude air bubbles completely and mix by inverting the bottle several times. When the precipitate settles leaving a clear supernatant above the manganese hydroxide floc, repeat the shaking a second time. When settling has produced at least 100 ml of clear supernatant, carefully remove the stopper and immediately add 2·0 ml of concentrated sulphuric acid, allowing the acid to run down the neck of the bottle; re-stopper and mix by gentle inversion until solution is complete. The iodine should be uniformly distributed throughout the bottle before decanting the amount needed for titration. This should correspond to 200 ml of original sample after correction has been made for the loss of sample by displacement with the reagents. Thus, when a total of 4 ml, 2 ml each of the manganous sulphate solution and the iodide-azide reagent, is added to a 300-ml bottle, the volume taken for titration should be

$$200 \times \frac{300}{300 - 4} = 203 \text{ ml}$$

Titrate with standard sodium thiosulphate solution to a pale straw colour. Add 1 to 2 ml of starch solution and continue the titration to the first disappearance of the blue colour. Subsequent recolourations due to the catalytic effect of nitrites or to the presence of traces of ferric salts which have not formed fluoride complexes should be disregarded.

50.4 Calculation

50.4.1 Dissolved oxygen, mg/l $= V$

where

V = volume in ml of standard sodium thiosulphate solution used in the titration.

50.4.2 If the results are to be expressed in terms of millilitres of oxygen gas at 0°C and 760 mm pressure, the dissolved oxygen content in terms of mg/l should be multiplied by 0·698.

50.4.3 *Expression of Results in Terms of Percent Saturation* — To express the results in terms of percent saturation at 760 mm pressure, the solubility value which is calculated by the method given in **50.4.3.1** may be used.

50.4.3.1 The solubility of dissolved oxygen in distilled water at an atmospheric pressure P mm, temperature t°C, and saturated vapour pressure u for the given temperature t°C, shall be calculated between the temperatures 0 and 30°C by equation (a) and between the temperatures 30 and 50°C by equation (b).

a) Solubility (ml of dissolved oxygen per litre of water)

$$= \frac{0{\cdot}678\ (P - u)}{(35 + t)}$$

b) Solubility (ml of dissolved oxygen per litre of water)

$$= \frac{0{\cdot}827\ (P - u)}{(49 + t)}$$

51. OXYGEN ABSORBED IN 4 HOURS

51.0 Outline of the Method — This is determined by estimating the amount of standard potassium permanganate solution consumed by the sample in 4 hours under specified conditions.

51.1 Test Temperature — This determination shall be carried out at a temperature of 37°C.

51.2 Reagents

51.2.1 *Stock Potassium Permanganate Solution* — Dissolve 3·951 g of potassium permanganate (dried at 105°C) in distilled water and make up to 1 000 ml. This solution shall be kept in the dark and its strength shall be checked periodically.

51.2.2 *Standard Potassium Permanganate Solution* — N/80. This solution shall be prepared immediately before use by suitable dilution of stock potassium permanganate solution. One millilitre of this solution is equivalent to 0·1 mg of oxygen.

51.2.3 *Dilute Sulphuric Acid* — Add slowly 50 ml of concentrated sulphuric acid to 130 ml of distilled water, cool and make up to 200 ml with distilled water. Add standard permanganate solution until a very faint pink colour persists after 4 hours.

51.2.4 *Potassium Iodide*

51.2.5 *Stock Sodium Thiosulphate Solution* — Dissolve 31·2 g of sodium thiosulphate and 6 g of sodium bicarbonate in water and make up to 1 000 ml.

51.2.6 *Standard Sodium Thiosulphate Solution* — N/80. This shall be prepared by suitable dilution of stock sodium thiosulphate solution. Before using the solution the strength shall be checked by titration with standard potassium permanganate solution.

51.2.7 *Starch Indicator Solution* — same as in **21.1.2**.

51.3 Procedure — Place 250 ml of the well-mixed sample into a clean, glass-stoppered bottle of 400 ml capacity. Add 10 ml of dilute sulphuric acid, followed by an accurately measured volume (*see* Note) of standard potassium permanganate solution. Mix by gentle rotation and place in a water-bath or incubator at 37°C for 4 hours. If the sample contains much suspended matter, it shall be mixed by gentle rotation several times during the period of incubation. At the end of 4 hours, cool to about 15°C, add a few crystals of potassium iodide and titrate in the bottle with standard sodium thiosulphate solution, using a few drops of starch indicator solution. A blank for oxygen absorbed in 3 minutes shall be carried out. Express the result to the nearest 0·05 mg/l.

NOTE — The measured volume of standard potassium permanganate solution taken shall be not less than 10 ml, but shall be such that at the end of 4 hours, the amount remaining unchanged is between 5 and 15 ml. If it is found that the volume required was anticipated incorrectly, the determination shall be repeated.

51.4 Calculation

$$\text{Oxygen absorbed in 4 hours, mg/l} = 0{\cdot}4\ V$$

where

V = volume in ml of standard potassium permanganate solution consumed in reaction with the sample.

52. TOTAL ORGANIC MATTER (OXYGEN CONSUMED)

52.0 Outline of the Method — This is determined by refluxing the sample with an excess of potassium dichromate in acid conditions and estimating by titration the amount of dichromate consumed.

52.1 Interference — Unstable samples should be tested without delay and samples containing settleable solids should be homogenized by suitable means for ease of representative sampling. Initial dilutions in volumetric flasks should be made on those samples having a high oxygen consumed value, in order to reduce the error which is inherent in measuring small

sample volumes. Chlorides are quantitatively oxidized by this procedure when silver sulphate is not used as a catalyst. In this case, a correction should be applied by determining chlorides on a separate sample and subtracting the calculated oxygen consumption of the chlorides from the result. Since 1 mg/l of chloride will consume 0·23 mg/l of oxygen, the correction is : mg/l of chloride × 0·23.

52.2 Reagents

52.2.1 *Standard Potassium Dichromate Solution* — 0·25 N.

52.2.2 *Concentrated Sulphuric Acid* — conforming to IS : 266-1961*.

52.2.3 *Standard Ferrous Ammonium Sulphate Solution* — 0·25 N. The solution shall be standardized daily against standard potassium dichromate solution.

52.2.4 *Ferroin Indicator Solution* — Dissolve 1·485 g of 1, 10-phenanthroline (monohydrate), together with 0·695 g of ferrous sulphate ($FeSO_4.7H_2O$) in distilled water and dilute to 100 ml.

52.2.5 *Silver Sulphate*

52.3 Procedure

52.3.1 Place a 50-ml sample, or an aliquot diluted to 50 ml with distilled water, in a 300-ml round-bottom flask fitted with ground-glass joint for attaching a condenser, and add 25 ml of standard potassium dichromate solution. Carefully add 75 ml of concentrated sulphuric acid, mixing after each addition.

> (*Caution* — The mixture shall be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask and the mixture may be blown out).

52.3.2 Attach the flask to the condenser and reflux the mixture for two hours. Pumice granules or glass beads should be added to the reflux mixture to prevent bumping. Cool and then wash down the condenser with about 25 ml of distilled water. In many cases, the 2-hour reflux period is not necessary. Therefore, with particular samples, the reflux period necessary to give the maximum oxygen consumed should be determined and the shorter period of refluxing may be permissible.

52.3.3 Transfer the contents to a 500-ml conical flask, washing out the reflux flask 4 to 5 times with distilled water. Dilute the mixture to about 350 ml and titrate the excess potassium dichromate with standard ferrous ammonium sulphate solution, using ferroin indicator. Generally, 2 to 3 drops of the indicator are used. The colour change is sharp, changing

*Specification for sulphuric acid (*revised*).

from a blue-green to a reddish-blue. The end point, however, will not be as sharp as in the standardization of the reagents because of the lower acid concentration. For this reason, it is necessary that the sample be diluted to at least 350 ml before the titration is carried out. A blank consisting of 50 ml of distilled water instead of the sample, together with the reagents, is refluxed in the same manner.

NOTE — More complete oxidation of many organic compounds, such as straight-chain alcohols and acids, may be obtained by the use of silver sulphate as a catalyst. One gram of silver sulphate is added directly to the mixture before refluxing.

52.4 Calculation

$$\text{Total organic matter (in terms of oxygen consumed), mg/l} = \frac{(A - B)\,N \times 8\,000}{V}$$

where

A = volume in ml of ferrous ammonium sulphate solution used in the titration in the blank,

B = volume in ml of ferrous ammonium sulphate solution used in the titration with the sample,

N = normality of standard ferrous ammonium sulphate solution, and

V = volume in ml of the sample taken for the test.

52.5 Precision and Accuracy — The method is quite precise and may be used on a wide variety of waters even though the back titration is less than 1 ml. For most organic compounds, the oxidation is 95 to 100 percent of the theoretical value. Using the silver sulphate catalyst, short straight-chain alcohols and acids are oxidized to the extent of 85 to 95 percent or better. Benzene, toluene and pyridine are not oxidized by either procedure.

53. BIOCHEMICAL OXYGEN DEMAND (BOD)

53.0 Outline of the Method — This is determined by measuring the loss in dissolved oxygen of the sample after incubating it for 5 days at 20°C.

53.1 Apparatus

53.1.1 *Glass Stoppered Bottles* — Narrow-neck bottles of about 250 ml capacity, with suitable water sealing.

53.2 Reagent

53.2.1 *Dilution Water* — Distilled water of good quality, free from metals, particularly copper, and aerated at 27°C. Add 0·3 g of sodium bicarbonate for every 1 000 ml of water.

53.3 Procedure — Adjust the temperature of a suitable portion of the well-mixed sample to 20°C. Remove oxygen or excess air by maintaining the sample under vacuum for 10 minutes with occasional shaking, the suction provided by an ordinary laboratory filter pump being adequate. Fill completely two glass-stoppered bottles with the sample after it has been treated as described above. Allow to stand for 15 minutes to avoid air bubbles and determine the dissolved oxygen in the one immediately and in the other after 5 days' incubation in darkness in the stoppered bottle, using an incubator or thermostat at 20°C, by the method described in **50.3**.

NOTE 1 — The dissolved oxygen content of the sample before incubation shall be approximately 9 mg/l or preferably less.

NOTE 2 — For samples of doubtful purity, put on 1 : 1 dilution as well, filling the narrow-neck bottle with a mixture of equal parts of the sample and of dilution water at 20°C. Further dilutions shall be used if necessary to ensure that not more than half the oxygen is consumed during the incubation. Determine the dissolved oxygen before and after incubation and calculate the result using the appropriate dilution factor.

53.4 Calculation

Biochemical oxygen demand (5 days at 20°C), mg/l = Initial dissolved oxygen content (mg/l) — dissolved oxygen content after incubation (mg/l).

54. PHENOLIC COMPOUNDS

54.0 Outline of the Method — Phenols are isolated by distillation under acidic conditions. The colour produced by phenol with aminoantipyrine at *p*H 10 is extracted with chloroform and measured in a spectrophotometer.

54.1 Apparatus

54.1.1 *Nessler Tubes* — 50 ml capacity.

54.2 Reagents

54.2.1 *Stock Phenol Solution* — Dissolve 1 g of phenol in distilled water and dilute to 1 litre. This solution shall be standardized by the procedure given in **54.3.1**.

54.2.2 *Standard Phenol Solution* — Prepared by suitable dilution of the standardized stock phenol solution so that 1 ml contains 0·000 1 mg of phenol.

54.2.3 *Standard Bromate-Bromide Solution* — Dissolve 2·784 g of potassium bromate and 10 g potassium bromide in distilled water and dilute to 1 litre.

54.2.4 *Concentrated Hydrochloric Acid* — conforming to **IS** : 265-1962*.

54.2.5 *Potassium Iodide*

54.2.6 *Standard Sodium Thiosulphate Solution* — exactly 0·025 N, freshly standardized.

54.2.7 *Starch Indicator Solution* — same as in **21.1.2.**

54.2.8 *Copper Sulphate Solution* — 10 percent *w/v.*

54.2.9 *Dilute Phosphoric Acid* — 1 : 10 *v/v.*

54.2.10 *Sodium Chloride*

54.2.11 *Chloroform*

54.2.12 *Sodium Hydroxide Solution* — approximately 0·1 N.

54.2.13 *Ammonium Chloride Solution* — approximately 5 percent *w/v.*

54.2.14 *Concentrated Ammonium Hydroxide* — sp gr 0·92.

54.2.15 *4-Aminoantipyrine Solution* — Dissolve 2·0 g of 4-aminoantipyrine in distilled water and dilute to 1 litre. This solution shall be prepared fresh every week.

54.2.16 *Potassium Ferricyanide Solution* — Dissolve 8 g in 100 ml of distilled water. This solution shall be prepared freshly before use.

54.3 Procedure

54.3.1 *Standardization of Stock Phenol Solution*

54.3.1.1 *Procedure* — Place approximately 100 ml of distilled water in a 500-ml glass-stoppered conical flask and add 50 ml of stock phenol solution. To this, add exactly 10 ml of bromate-bromide solution and about 5 ml of concentrated hydrochloric acid. Stopper and swirl the flask gently. If brown colour does not persist, add further exact 10-ml portions of bromate-bromide solution until brown colour persists. Normally, four 10-ml portions are required. Stopper, allow to stand for 10 minutes and add 1 g of potassium iodide. Titrate the liberated iodine with standard sodium thiosulphate solution using starch indicator solution. Carry out a blank determination in exactly the same manner, adding only 10 ml of bromate-bromide solution.

54.3.1.2 *Calculation*

$$\text{Phenol, mg/l} = 7{\cdot}835\left(\frac{AB}{10} - C\right)$$

*Specification for hydrochloric acid (*revised*).

where

A = volume in ml of standard sodium thiosulphate solution used in the blank determination,

B = volume in ml of bromate-bromide solution used with the sample, and

C = volume in ml of standard sodium thiosulphate solution used with the sample.

54.3.2 *Preliminary Distillation of Sample* — To 500 ml of the sample, add 5·0 ml of copper sulphate solution unless it has already been added as a preservative. Lower the *p*H of the solution to below 4·0 by adding dilute phosphoric acid; 0·7 ml is usually sufficient. Place the solution in an all-glass distillation apparatus and distil over 450 ml. Stop the distillation and when boiling ceases, add 50 ml of distilled water to the distilling flask and continue distillation until a total of 500 ml of distillate has been collected. If, at this stage, a distinct odour of other organic compounds is noticeable in the distillate or if an oily layer is noticeable, then further purification as given in **54.3.2.1** is necessary.

54.3.2.1 Acidify the distillate with 1 ml of dilute phosphoric acid and add 5·0 ml of copper sulphate solution. Transfer to a separating funnel and add 150 g of sodium chloride. Make three successive extractions with chloroform, using 50 ml in each extraction. In the first extraction, care shall be taken to see that all of the sodium chloride is in solution. Combine the chloroform extracts and extract them twice with 75-ml portions of sodium hydroxide solution. Combine the alkaline extracts and dilute to about 250 ml with distilled water. Heat on a water-bath until all the chloroform has been removed. Cool and dilute to 500 ml. Redistil as in **54.3.2** and use an aliquot of the final distillate obtained for colorimetric determination.

54.3.3 *Colorimetric Determination*

54.3.3.1 Determine by a preliminary determination a suitable aliquot of the distillate for colorimetric determination. For this purpose, carry out the test in Nessler tubes, comparing the colour obtained with a series of suitable standards. In this preliminary determination, chloroform extraction prescribed in **54.3.3.2** in the determination with the sample is not necessary.

54.3.3.2 Dilute an aliquot containing not more than 0·05 mg of phenol to 500 ml with distilled water and place in a glass-stoppered bottle. Prepare a blank of 500 ml of distilled water and a control standard consisting of 500 ml of standard phenol solution. Sometimes, the standard phenol solution gives too large an absorbance for getting a satisfactory reading on some spectrophotometers, in which case a more dilute standard phenol solution shall be used. To the sample, blank and the control standard, add 10 ml of ammonium chloride solution and adjust with concentrated

ammonium hydroxide to *p*H 10·0 ± 0·2. This usually requires 3·5 to 5·0 ml of concentrated ammonium hydroxide. Mix and then add exactly 3·0 ml of 4-aminoantipyrine solution. Mix again and add 3 ml of potassium ferricyanide solution. Mix thoroughly, allow to stand for 3 minutes and extract immediately with chloroform, making three successive extractions using 15, 10 and 5 ml of chloroform. Combine the chloroform extracts, filter and dilute to 25 ml with chloroform. Read the absorbance of the sample and the control standard against the blank in a spectrophotometer at 460 μm. If the absorbances are greater than 1·0 with a 5-cm cell, readings shall be taken with a 1-cm cell.

54.4 Calculation

$$\text{Phenolic compounds (as } C_6H_5OH\text{), mg/l} = \frac{1\,000\ w\ a_1}{a_2\ v}$$

where

w = amount in mg of phenol present in the control standard,

a_1 = absorbance in the sample,

a_2 = absorbance in the control standard, and

v = volume in ml of the sample taken for the test.

55. TANNINS

55.0 Outline of the Method — Tannins reduce phosphomolybdic and phosphotungstic acid to give a blue colour which is matched against that produced with a series of standard tannin solutions.

55.1 Apparatus

55.1.1 *Nessler Tubes* — 50 ml capacity.

55.2 Reagents

55.2.1 *Folin-Dennis Reagent* — Add 100 g of sodium tungstate, 10 g of phosphomolybdic acid and 50 ml of phosphoric acid (sp gr 1·75) to 750 ml of distilled water. Boil gently for 2 hours, cool and dilute to 1 litre.

55.2.2 *Sodium Hexametaphosphate Solution* — 25 percent *w/v*.

55.2.3 *Sodium Carbonate Solution* — 15 percent *w/v*.

55.2.4 *Standard Tannin Solution* — Dissolve 1·000 g of tannin in about 80 ml of distilled water and make to 100 ml in a graduated flask. Just before use, dilute 10 ml of the solution again to 1 litre. One millilitre of the diluted solution is equivalent to 0·1 mg of tannin.

55.3 Procedure — Measure 25 ml of the sample into a Nessler tube. Add 1 ml of Folin-Dennis reagent, mix, add 2 ml of sodium hexametaphosphate

solution, mix and allow to stand for 5 minutes. Add 20 ml of sodium carbonate solution, mix and allow to stand for a further 10 minutes. Into eleven Nessler tubes, measure 0, 0·25, 0·50, 0·75, 1·00, 1·25, 1·50, 1·75, 2·00, 2·25, 2·50 ml of standard tannin solution. Dilute each to 25 ml, then treat in the same manner as the sample. Compare the colour of the test solution with the colour of the standards.

55.4 Calculation

$$\text{Tannins, mg/l} = 1\,000\frac{W}{V}$$

where

W = amount in mg of tannin in the Nessler tube matching the colour obtained with the sample, and

V = volume in ml of the sample taken for the test.

56. CHLOROFORM EXTRACTABLE MATTER

56.1 Apparatus

56.1.1 *Stirring Apparatus* — The stirring apparatus shall be equipped with a non-corrodible impeller of the type having a hollow cross-tube with a hole at the bottom centre, or an impeller of equivalent efficiency. It shall be capable of operating at 1 250 to 1 750 rev/min in water and shall be of suitable size to enter a 1-litre wide-mouth conical flask.

56.2 Reagents

56.2.1 *Dilute Hydrochloric Acid* — Mix one volume of concentrated hydrochloric acid with nine volumes of water.

56.2.2 *Chloroform* — re-distilled.

56.3 Procedure — Take a suitable volume of the sample. Adjust with dilute hydrochloric acid the *p*H of the sample to a value between 3 and 4 and place in a 1-litre conical flask. Add 100 ml of chloroform to the flask and stir mechanically for 15 minutes at a rate of 1 250 to 1 750 rev/min. Remove the stirrer and allow time for the two phases to separate; then transfer the chloroform layer to a 500-ml separating funnel by means of a glass siphon. No lubricant shall be used on the stopcock of the funnel. Add 50 ml of chloroform to the conical flask and repeat the stirring for 15 minutes; then transfer the second portion of chloroform also to the same separating funnel. Draw off the chloroform layer from the separating funnel through a dry, fat- and oil-free filter paper into a 250-ml beaker. If there is any suspended matter at the interface, leave about 2 ml of the chloroform layer in the funnel. Add a fresh 20-ml portion of chloroform

directly to the funnel, shake, and then withdraw the chloroform, using it as a wash for the filter. Evaporate the chloroform to about 20 ml on a boiling water-bath; then transfer it quantitatively to a weighed platinum or silica evaporating dish. Again reduce the volume to 20 ml on a boiling water-bath; then continue the evaporation at room temperature, covering the dish with a ribbed watch-glass to protect the contents from contamination with dust. Weigh the dish periodically until constant weight is obtained.

56.4 Calculation

$$\text{Chloroform extractable matter, mg/l} = 1\,000\,\frac{W}{V}$$

where

W = weight in mg of the residue, and

V = volume in ml of the sample taken for the test.

57. CHLORINE DEMAND

57.0 General

57.0.1 Chlorine demand is that amount of chlorine which has to be added to water to reach the break point, that is, the point at which free residual chlorine will just be present under specific conditions of time and temperature. Because of the very varied purposes for which the water may be used it is not possible to fix the time of contact or temperature to be used for this test. The time and temperature chosen should be basd on the probable conditions applying in practice and the time and temperature shall be stated with the result.

57.0.2 *Outline of the Method* — The procedure for chlorine demand falls into two parts, firstly the chlorination of portions of the sample using various doses of chlorine both above and below the break point, and secondly the examination of the treated portions, after the required period of contact, in order to determine its content of total residual chlorine.

57.1 Procedure

57.1.1 Chlorinate several portions of the sample with varying doses of chlorine. Test the portions for total residual chlorine as prescribed in **45** and draw a break point curve as shown in Fig. 7. Three distinct types of curves are possible as shown in Fig. 7.

Type A — for a sample free from chlorine-absorbing matter. This curve has a slope of 45° commencing from the origin itself. This would indicate a chlorine demand equal to zero.

Type B — for samples containing free and saline ammonia as the chlorine-absorbing matter. This curve starts from the origin with a slope

of almost 45°, reaches a maximum, falls to a minimum and then rises again at 45°. The minimum is the break point.

Type C — for samples containing organic material including albuminoid ammonia as the chlorine-absorbing matter. This curve starts from the origin at a slope less than 45°, then becomes much less than 45° and finally continues at 45°. The point at which the curve commences to rise at 45° is the break point.

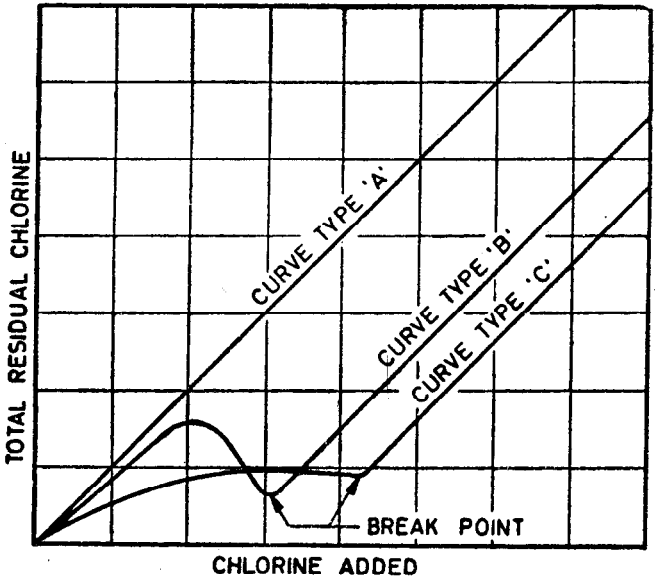

FIG. 7 BREAK POINT CURVE FOR CHLORINE DEMAND

58. ALPHA AND BETA PARTICLE ACTIVITY

58.0 General

58.0.1 The measurement of radiation-emitting alpha and beta particle activity has been described separately. The methods are, however, not applicable to samples containing alpha or beta-emitting radioelements like radon, C^{14} and H^3, which may be volatile under the conditions of the procedure for the preparation of samples for examination.

58.0.2 Since each radioelement has a characteristic rate of decay and energy of radiation, strict adherence to standard procedure is essential. The reagents and equipment used shall be free from radioactivity to preclude detrimental effects.

58.0.3 It is preferable to segregate the operation of monitoring radioactivity from other operations in the chemical laboratory. The instrument

used for radioactivity measurement shall be operated in a room where the temperature and humidity are not unduly high. A temperature less than 30°C and humidity less than 80 percent are usually considered satisfactory. Floors and work bench tops shall be of materials that can be cleaned easily.

58.0.4 Samples containing appreciable radioactivity shall be stored at a distance so as not to affect the instrument counter background (counting rate resulting from factors other than the activity of the sample and reagents used).

58.1 Collection of Samples — The principles of sampling described under **2** shall also apply to sampling for radioactivity examination. But as radioactive elements have a tendency to adhere to the surface of glassware, polyethylene containers are preferred for sampling. Preservation may alter the distribution of radioactivity in a sample and hence it is better to determine the activity soon after collection of sample. The addition of acids or complexing agents as preservatives may be done when absolutely necessary so as to obtain homogeneity of sample. The need for such addition is best indicated by the chemical nature of the radioelement and compounds present.

58.2 Alpha Particle Radioactivity

58.2.0 *Principle* — The sample is evaporated to dryness and the alpha particle activity measured by either a proportional or scintillation counter, consisting of a detecting device, amplifier, power supply and scaler. The background counting rate should be as low as possible in order to get good sensitivity for the instrument.

58.2.0.1 The method is applicable to alpha emitters having energies above 3·9 Mev and at radioactivity level value above 0·5 pc/ml.

58.2.1 *Apparatus*

58.2.1.1 *Alpha particle counter* — consisting of a proportional detector, either windowless or thin window type, or scintillation detector.

58.2.1.2 *Scaler*

58.2.1.3 *Sample mounting discs or dishes* — Flat bottomed, diameter slightly less than the inside diameter of the detector, made of non-corrodible material like platinum or stainless steel. The dishes shall have 3 mm high side walls with the angle between dish bottom and side not less than 120°

58.2.1.4 *Infrared heat lamp or heater* — adjustable.

58.2.2 *Reagents*

58.2.2.1 *Concentrated nitric acid*

58.2.2.2 *Dilute nitric acid* — 1 : 30 *v/v*.

58.2.3 *Establishing Counter Controls*

58.2.3.1 Set the instrument to working according to manufacturer's instructions. Place the counter control standard (*see* Note) in the detector, set the sensitivity control near its maximum and the count switch to ' count ' position.

NOTE — Any commercially available alpha-emitting radio-nuclide having a half life sufficiently long to justify neglecting decay corrections may be used as counter control standard.

58.2.3.2 Slowly increase the voltage until the first counts are observed and record the ' threshold ' voltage. Increase the voltage in steps of about 25 V and find out the counting rate at each voltage for four or more settings of the sensitivity control (*see* Note). Measure also the background counting rate at each of the settings using an empty sample mounting dish in place of the standard.

NOTE — The counting rate should initially rise with increase in voltage, then for at least some of the settings of the sensitivity control it remains fairly constant in value, and finally rises again.

58.2.3.3 Plot the gross counting rate of the standard against the voltage. Plot also the ratio of the square of the net counting rate of the standard to the background counting rate against the voltage for each of the settings of the sensitivity control. Find out from the graphs the optimum conditions for operation of the instrument by selecting values of the high voltage and sensitivity adjustments that correspond to a point lying on the plateau of the counting rate *versus* voltage curve and near the maximum value of the ratio of the square of the net counting rate to background counting rate.

58.2.3.4 Use control charts to ensure uniform daily operation of the instrument. Also, check daily the counting rate of the control standard and background. Regulate the room temperature without any appreciable variation for satisfactory performance.

58.2.4 *Determination of Efficiency Factor of the Counter*

58.2.4.1 Place a known quantity of alpha standard (approximately $5 \times 10^{-3} \mu c$) into a volume of distilled water sufficient to dissolve salts equivalent to those of the test sample and prepare for counting as directed under **58.2.5**. Purified natural uranium of which the specific activity is 1·50 disintegration per minute per microgram (0·676 pc/μg) has been found satisfactory for this purpose.

58.2.4.2 Count for a length of time required to produce satisfactory reliability. The efficiency factor is then expressed as a percentage of the disintegration rate of the reference standard.

NOTE — The evaporation, mounting, counting and density of plate solids of the reference standard shall be identical with those of the test samples throughout the experiment.

58.2.5 *Procedure*

58.2.5.1 Place an appropriate volume of the sample (so as to give not more than 5 mg of the residue for each cm^2 of the counting area) in a beaker, add 3 ml of concentrated nitric acid for each 100 ml and evaporate, without spattering, to 1 to 2 ml. Quantitatively transfer to the mounting dish and evaporate to dryness without spattering by boiling under controlled heat or with an infrared heat lamp. Uniform spreading of the residue is necessary. Dry at 103 to 105°C in an oven, cool and store in a desiccator until taken up for counting.

NOTE — When large volumes of samples are used, transfer to smaller beakers as it gets evaporated for an easy final transfer to the mounting dish. Use dilute nitric acid for all transfers.

58.2.5.2 Place the sample in the counter and count for a time interval sufficient to attain reliability (about 2 hours). Record the reading of the register and any other indication of accumulated counts.

58.2.5.3 Report the results in terms of the alpha disintegration rate using the efficiency determined by calibration of the standard.

58.2.6 *Calculation*

a) Alpha activity (C), cpm/ml $= \frac{1}{V}\left(\frac{A}{t} - B\right)$

where

cpm = net counts per minute,

A = total count accumulated,

B = background counts per minute,

t = time of counting in minutes, and

V = volume in ml of sample taken for the test.

b) Alpha disintegration rate, dpm/ml $= C/E$

where

dpm = disintegrations per minute,

C = alpha activity of the test sample in cpm/ml, and

E = efficiency of the counter (fraction)

$$\left(E = \frac{\text{observed counts per minute}}{\text{calculated disintegrations per minute}} \times 100 \right)$$

c) To convert the alpha disintegration rate (dpm/ml) to alpha emitters in terms of microcuries (μc), calculate as below:

$$\text{Alpha emitters, } \mu c/ml = \frac{\text{dpm/ml}}{2{\cdot}22 \times 10^6}$$

58.3 Beta Particle Radioactivity

58.3.0 *Principle* — The sample is evaporated to dryness and the beta particle activity measured by the Geiger-Muller or proportional counters composed of a detecting device and combined amplifier, power supply and scaler. The proportional type counter is preferable where the range of counting rates is wide (10 to 80 000 counts per minute) because of a shorter resolving time and greater stability of the instrument. The background counting rate should be as low as possible to get good sensitivity for the instrument.

58.3.0.1 The method is applicable to beta emitters having maximum energies above 0·1 Mev and at radioactivity levels about 0·5 pc/ml. The method can be used for either absolute or relative determination. For reliable measurements, the variables should be kept constant for test samples and standard while counting.

58.3.0.2 Materials interposed between the test sample and the instrument detector and also increasing density in the sample containing beta emitters produces significant loss in sample counting rates. Most of the beta radiation counters are sensitive to alpha, gamma and X-ray radiations and the effect of these interfering radiations on the beta counting rate could be evaluated with external type counters using appropriate absorbers.

58.3.1 *Apparatus*

58.3.1.1 *Beta particle counter* — consisting of either of the following types of commercially available detectors:

a) *The end window Geiger-Muller tube*

or

b) *The internal or external gas flow chamber*

58.3.1.2 *Detector shield* — an external radiation shield made of massive metal equivalent to approximately 5 cm of lead and lined with a 3 mm thickness of aluminium. The shield should have a door or port for inserting and removing specimens.

58.3.1.3 *Scaler*

58.3.1.4 *Sample mounting dishes* — same as **58.2.1.3.**

58.3.1.5 *Alpha particle absorber* — made of aluminium or plastic, of suitable diameter and having a uniform density such that the total absorbing medium (air plus window plus absorber) between sample and sensitive volume of detector is equal to about 7 mg/cm^2 of aluminium. This absorber shall not be used when counting beta activity with maximum energies below 0·35 Mev because of a high loss of counting

rate by absorption. The alpha particle absorber is not recommended for use with internal beta particle detectors especially when the composition or radioactivity levels of samples might vary significantly.

58.3.2 *Reagent*

58.3.2.1 *Concentrated nitric acid*

58.3.3 *Establishing Counter Controls*

58.3.3.1 Set the instrument to working according to manufacturer's instructions. Place the counter control standard having an approximate disintegration rate of 10 000 disintegrations per minute in the counting position close to the detector and turn the count switch to 'count' position.

NOTE — Any available radio-nuclide having a high percentage of beta particle emission, a half life sufficiently long to justify neglecting decay corrections and a maximum beta particle energy about 0·5 Mev may be used as counter control standard.

58.3.3.2 Slowly increase the high voltage until the first counts are observed and record the 'threshold' voltage. Raise the voltage 20 or 25 V above threshold, turn 'count' switch off, re-set the scaler to zero and again find out the counting rate. Advance the voltage in equal increments of 20 or 25 V determining the counting rate at each voltage. Measure also the background counting rate at each of the settings using an empty sample mounting dish in place of the standard.

NOTE — The counting rate should rise initially, reach an approximately constant value and then increase rapidly. The operating time at voltages above the plateau should be minimized to avoid extensive arcing of the detector. If the plateau is 150 V in length, additional measurements are not necessary.

58.3.3.3 Plot the counting rate of the standard against voltage. The voltage setting that corresponds to a value approximately 75 V above the 'knee' of the curve shall be used as the operating voltage, provided this voltage is 50 V below the highest voltage on the plateau; otherwise the operating voltage shall be that at approximately midpoint of the plateau. A plateau slope of less than 3 percent for 100 V is desirable and between 3 to 6 percent may be considered tolerable if a stable power supply is used. The voltage plateau and operating voltage shall be checked regularly and after any major adjustment of the instrument.

58.3.3.4 Use control charts to ensure uniform daily operation of the instrument. Check daily the counting rate of the control standard and the background.

58.3.4 *Determination of Efficiency Factor of the Counter*

58.3.4.1 Place a known amount of beta standard (strontium-90 or yttrium-90) (approximately $5 \times 10^{-3}\mu c$) into a volume of water sufficient to dissolve salts equivalent to those of the test sample and prepare for counting as directed under **58.3.5.**

58.3.4.2 Count for a length of time required to produce satisfactory reliability. The combined efficiency factor is then expressed as a percentage of the disintegration rate of the reference standard.

NOTE 1 — The evaporation, mounting, counting and density of plate solids of the reference standard shall be identical with those of the test samples throughout the experiment.

NOTE 2 — The reference standard may be covered by a thin aluminium or plastic cover of sufficient thickness to exclude any alpha particles originating from the source.

58.3.5 *Procedure*

58.3.5.1 Place an appropriate volume of the sample (so as to give not more than 20 mg of the residue for each cm^2 of counting area) in a beaker, add concentrated nitric acid to make 0·5 N and evaporate, without spattering, to 1 to 2 ml (*see* Note under **58.2.5.1**). Quantitatively transfer to the mounting dish and evaporate to dryness without spattering by boiling under controlled heat or with an infrared heat lamp. Uniform spreading of the residue is necessary. Dry in an oven at 103 to 105°C, cool and store in a desiccator until taken for counting.

58.3.5.2 Place the sample in the counter and count for a time interval sufficient to attain reliability (about 30 minutes).

58.3.5.3 Report the result in terms of beta disintegration rate using the efficiency determined by calibration of the standard.

58.3.6 *Calculation*

a) Beta activity (c), $\text{cpm/ml} = \frac{1}{V}\left(\frac{A}{t} - B\right)$

where

cpm = net counts per minute,
A = total count accumulated,
B = background counts per minute,
t = time of counting in minutes, and
V = volume in ml of sample taken for the test.

b) Beta disintegration rate, $\text{dpm/ml} = C/EX$

where

dpm = disintegrations per minute,
C = beta activity of test sample in cpm/ml, and
EX = efficiency of the counter (fraction)

$$\left(EX = \frac{\text{observed counts per minute}}{\text{calculated disintegration per minute}} \times 100\right)$$

c) To convert the beta disintegration rate (dpm/ml) to beta emitters in terms of microcuries (μc), calculate as below:

$$\text{Beta emitters, } \mu c/\text{ml} = \frac{\text{dpm/ml}}{2{\cdot}22 \times 10^6}$$

59. OILS AND GREASE

59.0 Outline of the Method — The oils and grease are extracted by an organic solvent. The solvent is distilled off and the weight of the extracted matter determined. Some extractables, especially unsaturated fats and fatty acids, oxidize rapidly; hence, special precautions regarding temperature and solvent vapour displacement are necessary to minimize this effect.

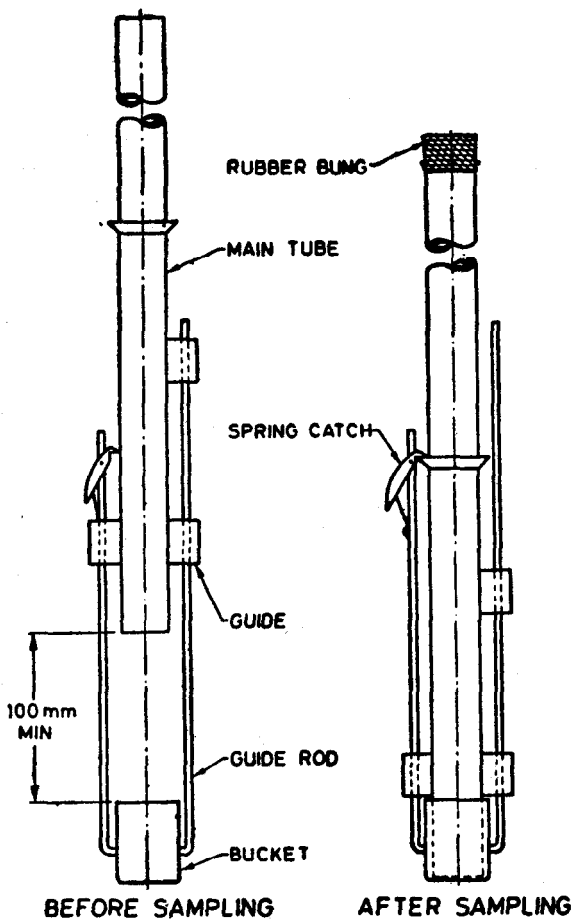

FIG. 8 SAMPLING TUBE

59.1 Sampling — The most satisfactory method of sampling two-phase liquids is to use a sampling tube that is capable of withdrawing a complete section of the water as it flows in a rectangular culvert or trough; in most instances, however, water will have to be sampled from the outfall of a pipe or from a stream and in these circumstances some of the water should first be collected in a large cylindrical vessel having a capacity of 10 to 15 litres. A sectional sampling tube should be used to withdraw the test sample from this. A sampling tube suitable for sampling waters that do not contain highly viscous matter (for example, tar) is shown in Fig. 8. The sampler consists of a heavy-gauge brass tube, 1 m long, with an outside diameter of 40 mm. Over one end of the tube is fitted a brass bucket made from a piece of tube 50 mm long and sealed at one end. The bucket has an internal diameter 1·5 mm greater than the outside diameter of the main tube. To the opposite sides of the bucket are brazed two brass rods, 6 mm in diameter, which pass through guides brazed to the sides of the main tube. The rods are so arranged that the top of the bucket can be withdrawn to a distance of not less than 10 cm from the bottom of the main tube, and they guide the bucket into a position covering the end of the tube when it is pushed back again. A suitable spring catch is provided on one of the guide rods so that the bucket is automatically locked into the top position when it is raised to its highest point. The open end of the sampling tube is fitted with a rubber bung.

59.1.1 To take a sectional sample, the spring catch is released and the bucket is drawn as far away as possible from the end of the main tube. The rubber bung is withdrawn from the other end. The tube is lowered vertically through the liquid to be sampled until the bottom of the bucket rests on the bottom of the culvert or of the vessel that has been filled with the water. The main tube is then pushed down, guided by the brass rods, to the limit of its travel, whereupon the spring catch locks the bucket in the raised position covering the end of the tube. The rubber bung is tightly inserted in the open end and the tube is withdrawn. The outside of the sampler is wiped free of adhering liquid, the bucket and the lower part of the tube are inserted into a wide-mouthed bottle of suitable capacity, and the rubber bung is removed. The sample section of the liquid will flow into the bottle leaving a small quantity of liquid in the bucket. The tube is then tilted, so that this liquid is added to the main bulk of the sample. The operation is repeated until sufficient quantity has been collected. At least 25 mm of air space should be left between the top level of the liquid and the stopper of the bottle.

59.2 Storage of Sample — Since many oils and hydrocarbons are utilized by bacteria, storage is obviously detrimental. However, if it becomes necessary to store the sample before analysis is taken up, the samples should be acidified with dilute sulphuric acid (1 : 1), 5 ml/l, of the sample, to inhibit bacterial activity.

59.3 Apparatus

59.3.1 *Separating Funnels* — of 1·5 to 2 litre capacity. The stopper or stop cock should not be lubricated with matter soluble in petroleum ether.

59.4 Reagents

59.4.1 *Dilute Hydrochloric Acid* — 1 : 1.

59.4.2 *Light Petroleum* (*Petroleum Ether*) — boiling range 40 to 60°C.

59.5 Procedure

59.5.1 Place the sample, usually 1 litre, in a separating funnel of sufficient size to allow the addition of acid and solvent, and still have space for proper agitation. Acidify the sample with dilute hydrochloric acid, 5 ml/l, of the sample. Rinse the sample bottle carefully with 15 ml of petroleum ether and add the ether washings to the separating funnel. Add an additional 25 ml of ether to the sample bottle, rotate the ether in the sample bottle and add the ether to the separating funnel. Shake vigorously for 2 minutes. Allow the ether layer to separate. Withdraw the aqueous portion of the sample into a clean container, and transfer the solvent layer into a clean, tared distilling flask capable of holding at least three volumes of solvent (*see* Note). If a clear ether layer cannot be obtained, filter the solvent layer into the tared distilling flask through a funnel containing an ether moistened filter paper (Whatman No. 40 or equivalent). The filter paper should be washed with petroleum ether after folding to avoid inclusion of skin oils. Use as small a funnel and filter paper as practical.

NOTE — While transferring the solvent layer from the separating funnel, a small quantity of it remains at the stem of the separating funnel; it is advisable to wash it with a few millilitres of the solvent and to add the washings to the solvent layer.

59.5.2 Return the aqueous portion of the sample to the separating funnel, rinsing the container with 15 ml of ether. Add the ether washings and an additional 25 ml of ether to the separating funnel, and agitate for another 2 minutes. Allow the solvent layer to separate and discard the aqueous phase. Add the ether extract to the tared distilling flask and rinse the separating funnel with 20 ml of ether. Add the ether washings to the tared distilling flask. After all the ether from the two extractions and the final rinsing are included, wash down the funnel and filter paper twice with fresh 5-ml increments of petroleum ether.

59.5.3 Distil off all but approximately 10 ml of the ether extract on a water-bath or an electric-heating mantle, observing necessary safety precautions and keeping the heat source at about 70°C. Disconnect the condenser and boil off the remaining solvent from the tared flask at the same temperature. Dry on a water-bath or steam-bath. When dry, lay the flask on its side to facilitate the removal of solvent vapour. Introduce

approximately three volumes of dry illuminating gas or nitrogen into the flask to displace the solvent vapour. Cool in a desiccator for 30 minutes and weigh.

59.6 Calculation

$$\text{Oils and grease, mg/l} = \frac{1\,000\ W}{V}$$

where

W = weight in mg of the residue in the flask, and

V = volume in ml of the sample taken for the test.

59.6.1 Express the result to the nearest milligram.

APPENDIX A

(*Clauses* 2.1.4 *and* 2.9.1)

INFORMATION TO BE SUPPLIED ALONG WITH SAMPLES

A-1. While submitting samples, the following particulars shall be supplied along with the samples:

a) Name and address of person requesting the examination;

b) Name, designation or other identification particulars of the person drawing samples;

c) Date and time of collection and despatch;

d) Reasons for examination and whether it is a routine sample or otherwise;

e) Source of water (well, spring, stream, public supply, etc);

f) Exact place from which sample was taken. If from a tap, whether the sample was drawn through a cistern, or directly from the main;

g) The method of purification and sterilization used, if any; give details of dose of chemicals, point of application, quantity treated, etc;

h) Temperature of the sample;

j) Weather at the time of collection, and particulars of recent rainfall;

k) Whether the water becomes affected in appearance, odour or taste after heavy rains;

m) In the case of samples of industrial process water, whether cooling coils have been used and if so, the temperature of the sample before cooling;

n) If sample has been taken from a well, then:

1) Depth of well, and of water surface from ground level;

2) Whether covered or uncovered, and nature, material, and construction of the cover;

3) Whether newly constructed or with any recent alterations which might affect the condition of the water;

4) Type of construction — (i) bricks set dry or in cement; (ii) cement or cylinder lined, and whether puddled outside the lining; (iii) depth of lining; (iv) whether bricked above ground surface, if so, height of coping; (v) presence and extent of apron; and (vi) method of pumping or other means of raising water;

5) Proximity of drains, cesspools or other possible sources of pollution, and distance from source;

6) Any discoloration of the sides of the well, or other visible indication of pollution;

7) Nature of subsoil and water-bearing stratum;

NOTE — When available, a section or drawing of the well and general surroundings should be furnished.

p) If sample has been taken from a spring, then:

1) Stratum from which it issues;

2) Whether sample has been taken direct from spring or from a collecting chamber. If from latter, mode of construction of the chamber;

q) If sample has been taken from a river or stream, then:

1) Depth below surface at which sample was taken;

2) Whether sample was taken from the middle or side;

3) Whether the level of water is above or below the average;

4) Conditions of weather at the time of sampling, and particulars of any recent rainfall or flood conditions;

5) Observations with reference to any possible sources of pollution in the vicinity and if so, its approximate distance from sampling point; and

r) Results of field tests made on the sample.

APPENDIX B

(*Clause* 8.2.1)

PREPARATION OF INDICATORS AND BUFFER SOLUTIONS FOR DETERMINATION OF *p*H

B-1. INDICATORS

B-1.1 A list of suitable indicators is given in Table 5 together with their *p*H range, colour change and methods of preparation.

B-1.1.1 *Universal Indicator* — Dissolve 0·05 g of methyl orange, 0·15 g of methyl red, 0·3 g of bromothymol blue and 0·35 g of phenolphthalein in one litre of alcohol (66 percent). The colour changes are:

*p*H	*Colour*
up to 3	red
4	orange-red
5	orange
6	yellow
7	yellowish-green
8	greenish-blue
9	blue
10	violet
11	reddish-violet

TABLE 5 INDICATORS

(*Clause* B-1.1)

Sl No.	Name of Indicator	*p*H Range	Colour Change	Method of Preparation
(1)	(2)	(3)	(4)	(5)
i)	Thymol blue (acid range)	1·2 to 2·8	Red to yellow	Triturate 0·10 g in 10·75 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
ii)	Bromophenol blue	3·0 ,, 4·6	Yellow to blue violet	Triturate 0·10 g in 7·45 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
iii)	Bromocresol green	3·8 ,, 5·4	Yellow to blue	Triturate 0·10 g in 7·15 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
iv)	Methyl red	4·2 ,, 6·3	Red to yellow	Triturate 0·10 g in 18·60 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
v)	Bromocresol purple	5·2 ,, 6·8	Yellow to blue violet	Triturate 0·10 g in 9·25 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
vi)	Bromothymol blue	6·0 ,, 7·6	Yellow to blue	Triturate 0·10 g in 8·00 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
vii)	Phenol red	6·8 ,, 8·4	Yellow to red	Triturate 0·10 g in 14·20 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
viii)	Cresol red	7·2 ,, 8·8	Yellow to red	Triturate 0·10 g in 13·10 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
ix)	Thymol blue (alkali range)	8·0 ,, 9·6	Yellow to blue	Triturate 0·10 g in 10·75 ml of N/50 sodium hydroxide solution and dilute with distilled water to 250 ml
x)	Thymolphthalein	9·3 ,, 10·5	Colourless to blue	Dissolve 0·10 g in 100 ml of rectified spirit (conforming to IS : 323-1959*)
xi)	Thymol violet	9·0 ,, 13·0	Yellow to green to violet	Dissolve 0·01 g of tropaeolin 0 in 100 ml of distilled water. Dissolve 0·04 g of thymolphthalein in a mixture of 50 ml of rectified spirit and 50 ml of water. Mix one part of tropaeolin 0 solution with 4 parts of thymolphthalein solution.

*Specification for rectified spirit (*revised*).

B-2. STANDARD BUFFER SOLUTIONS

B-2.1 Standard buffer solutions prepared as given below shall be kept in bottles made of alkali-free glass (conforming to Type 1 of IS : 2303-1963*) or of polyethylene, and shall not be used later than three months after preparation.

a) *Solutions from* pH 1·2 *to* pH 2·2 shall be prepared by mixing 50 ml of M/5 potassium chloride solution with the specified volumes of N/5 hydrochloric acid as given below and diluting with distilled water to 200 ml.

pH	*Volume of* N/5 *Hydrochloric Acid* (in ml)
1·2	64·5
1·4	41·5
1·6	26·3
1·8	16·6
2·0	10·6
2·2	6·7

b) *Solutions from* pH 2·2 *to* pH 3·8 shall be prepared by mixing 50 ml of M/5 potassium hydrogen phthalate solution with the specified volumes of N/5 hydrochloric acid as given below and diluting with distilled water to 200 ml.

pH	*Volume of* N/5 *Hydrochloric Acid* (in ml)
2·2	46·7
2·4	39·6
2·6	33·0
2·8	26·4
3·0	20·3
3·2	14·7
3·4	9·9
3·6	6·0
3·8	2·6

c) *Solutions from* pH 4·0 *to* pH 6·2 shall be prepared by mixing 50 ml of M/5 potassium hydrogen phthalate solution with specified

*Methods of grading glass for alkalinity.

volumes of N/5 sodium hydroxide solution as given below and diluting with distilled water to 200 ml.

*p*H	*Volume of* N/5 *Sodium Hydroxide Solution* (in ml)
4·0	0·4
4·2	3·7
4·4	7·5
4·6	12·2
4·8	17·7
5·0	23·8
5·2	30·0
5·4	35·4
5·6	39·8
5·8	43·0
6·0	45·4
6·2	47·0

d) *Solution from* *p*H 5·8 *to* *p*H 8·0 shall be prepared by mixing 50 ml of M/5 potassium dihydrogen phosphate solution with the specified volumes of N/5 sodium hydroxide solution as given below and diluting with distilled water to 200 ml.

*p*H	*Volume of* N/5 *Solution Hydroxide Solution* (in ml)
5·8	3·7
6·0	5·7
6·2	8·6
6·4	12·6
6·6	17·8
6·8	23·5
7·0	29·6
7·2	35·0
7·4	39·5
7·6	42·8
7·8	45·2
8·0	46·8

e) *Solutions from* pH 7·8 *to* pH 10·0 shall be prepared by mixing 50 ml of M/5 boric acid-potassium chloride solution (prepared by dissolving 12·369 g of boric acid and 14·911 g of potassium chloride is distilled water and making the final volume to 1 000 ml) with the specified volumes of N/5 sodium hydroxide solution as given below and diluting with distilled water to 200 ml.

*p*H	*Volume of* N/5 *Sodium Hydroxide Solution* (in ml)
7·8	2·6
8·0	4·0
8·2	5·9
8·4	8·5
8·6	12·0
8·8	16·3
9·0	21·3
9·2	26·7
9·4	32·0
9·6	36·8
9·8	40·8
10·0	43·9

f) *Solutions from* pH 8·4 *to* pH 12·8 shall be prepared by mixing X ml of M/10 glycine-sodium chloride solution (containing 7·505 g of glycine and 5·850 g of sodium chloride per litre of the solution) and Y ml of N/10 sodium hydroxide solution as specified below:

*p*H	*X* ml *Glycine-Sodium Chloride Solution*	*Y* ml *Sodium Hydroxide Solution*
8·4	9·5	0·5
8·8	9·0	1·0
9·2	8·0	2·0
9·6	7·0	3·0
10·0	6·0	4·0
10·3	5·5	4·5
10·9	5·1	4·9
11·1	5·0	5·0
11·4	4·9	5·1
11·9	4·5	5·5
12·2	4·0	6·0
12·5	3·0	7·0
12·7	2·0	8·0
12·8	1·0	9·0

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TO
IS : 3025-1964 METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER USED IN INDUSTRY

Addenda

(*Page* 12, *clause* 3.6) — Add the following new clause after 3.6:

3.7 Reporting of Results — Unless otherwise required by the relevant standard for water quality, in reporting the results of analysis of water according to the methods prescribed, the results shall be reported to the number of significant places given below:

Test Result	*Report*
Less than 0·1	To the nearest 0·001 unit
0·1 to 1·0	,, ,, ,, 0·01 ,,
More than 1·0 to 10	,, ,, ,, 0·1 ,,
11 to 100	,, ,, ,, 1 ,,
101 to 500	,, ,, ,, 5 ,,
501 and above	,, ,, ,, 10 ,,

(CDC 26)

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