

*Indian Standard*

**METHOD FOR COLORIMETRIC  
ANALYSIS OF HYDRAULIC CEMENT**

(First Reprint JUNE 1991)

UDC 666.94.015.57 : 543.432

© Copyright 1988

**BUREAU OF INDIAN STANDARDS**  
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG  
NEW DELHI 110002

# Indian Standard

## METHOD FOR COLORIMETRIC ANALYSIS OF HYDRAULIC CEMENT

### 0. FOREWORD

**0.1** This Indian Standard was adopted by the Bureau of Indian Standards on 20 June 1988, after the draft finalized by the Cement and Concrete Sectional Committee had been approved by the Civil Engineering Division Council.

**0.2** For chemical analysis of hydraulic cement, the general practice is to follow the conventional gravimetric and volumetric methods. These methods are tedious and time consuming. The advent of instruments based upon electromagnetic radiations has brought speed and accuracy to analytical methods. Adoption of such methods would help in rapid analysis of major and minor constituents of cement for quality control purposes by the cement industry. With this in view, the Cement and Concrete Sectional Committee considered it necessary to bring out a standard covering the methods for colorimetric analysis of hydraulic cement. Colorimetric methods of analysis of hydraulic cement

are being introduced as alternate rapid methods of analysis and in case of any dispute, gravimetric methods described in IS : 4032-1985\* shall be taken as referee methods. This standard lays down the procedure for conducting colorimetric analysis of major and minor constituents of different varieties of hydraulic cement.

**0.3** For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS : 2-1960†. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

\*Method of chemical analysis of hydraulic cement (first revision).

†Rules for rounding off numerical values (revised).

### 1. SCOPE

**1.1** This standard covers the colorimetric procedures for chemical analysis of different varieties of hydraulic cement.

**1.2** This standard covers the colorimetric determination of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{SO}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  and chloride in cement.

### 2. SAMPLING

**2.1** The samples of the cement shall be taken according to the requirements of IS : 3535-1986\* and the relevant standard specification for the type of cement being tested. The representative sample of the cement selected as above shall be thoroughly mixed before using.

### 3. REPRODUCIBILITY OF RESULTS

**3.1** Blank determinations shall be made on reagents for each constituent in the cement and the corrections shall be applied where necessary. In all cases check determinations shall be made and repeated if satisfactory checks are not obtained. The difference between check determinations shall not exceed 0.15 percent for silica and calcium oxide, and 0.1 percent for all other

\*Methods of sampling hydraulic cements (first revision).

constituents, except for chloride where difference between check determinations shall not exceed 0.02 percent.

### 4. APPARATUS

**4.1 Spectrophotometer** — Single or double beam, recording or non-recording type with a wavelength range of 350-950  $\text{m}\mu$  capable of providing band width of 10  $\text{m}\mu$  with wavelength accuracy of  $\pm 1 \text{ m}\mu$  and wavelength least count of 1  $\text{m}\mu$  fitted with optical glass cells and voltage stabilizer.

**4.2 Balance** — Analytical chemical balance capable of weighing up to 0.1 mg.

**4.3 Glassware** — All glasswares used in measurements shall be 'A' certified.

**4.4 Burner** — Bunsen burner.

**4.5 Muffle Furnace** — It shall be capable of operating up to 1100°C.

**4.6 Platinum Crucible** — Capacity 20 ml.

**4.7 Nickel/Zirconium Crucible** — Capacity 20 ml.

### 5. USE OF FILTER PAPERS

**5.1** In the methods prescribed in this standard, relative numbers of Whatman filter paper only

have been prescribed since these are commonly used. However, any other suitable brand of filter papers with equivalent porosity may be used.

## 6. CHEMICAL ANALYSIS OF CEMENTS

**6.1 Reagents and Special Solutions** — Unless specified otherwise, pure chemicals of analytical reagent grade shall be employed in tests, and distilled water (see IS : 1070-1977\*) shall be used where the use of water as a reagent is intended. The following reagents and special solutions of analytical reagent grades are required (see IS : 2263-1979† and IS : 2316-1968‡)

### 6.1.1 Reagents

- 6.1.1.1 Acetic acid — glacial.
- 6.1.1.2 Acetone
- 6.1.1.3 Aluminium metal
- 6.1.1.4 Ammonium hydroxide — sp gr 0.90.
- 6.1.1.5 Ammonium sulphates — solid.
- 6.1.1.6 Ammonium vanadate — solid.
- 6.1.1.7 Amyl alcohol
- 6.1.1.8 Boric acid — solid
- 6.1.1.9 Calcium carbonate — solid.
- 6.1.1.10 Diammonium hydrogen orthophosphate — solid.
- 6.1.1.11 Dimethyl formamide solution
- 6.1.1.12 Ethyl alcohol — of 99 percent purity.
- 6.1.1.13 Ferric alum — solid.
- 6.1.1.14 Ferric nitrate — solid.
- 6.1.1.15 Gelatin — solid.
- 6.1.1.16 Hydrochloric acid — sp gr 1.18 (conforming to IS : 265-1976§).
- 6.1.1.17 Hydroxylamine hydrochloride — solid.
- 6.1.1.18 Iron metal
- 6.1.1.19 Manganese powder
- 6.1.1.20 Magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) — solid.
- 6.1.1.21 Mercuric thiocyanate — solid.
- 6.1.1.22 Phosphoric acid — 85 percent (1 : 3 by volume).
- 6.1.1.23 Polyvinyl alcohol — solid.
- 6.1.1.24 Potassium chloride — solid.
- 6.1.1.25 Potassium titanium oxalate — solid.
- 6.1.1.26 Potassium periodate — solid.
- 6.1.1.27 Potassium sulphate — solid.

\*Specification for water for general laboratory use (second revision).

†Methods of preparation of indicator solutions (first revision).

‡Methods of preparation of standard solutions for colorimetric and volumetric analysis (first revision).

§Specification for hydrochloric acid (second revision).

6.1.1.28 Quartz — solid, of 99.5 percent purity.

6.1.1.29 Silver nitrate — solid.

6.1.1.30 Sodium acetate trihydrate — solid.

6.1.1.31 Sodium carbonate — anhydrous.

6.1.1.32 Sodium hydroxide — pellets.

6.1.1.33 Sodium sulphide — solid flakes.

6.1.1.34 Sodium tetra-borate — solid.

6.1.1.35 Sulphuric acid — sp gr 1.84 (conforming to IS : 266-1977\*).

6.1.1.36 Triethanolamine

**6.1.2 Dilute Solutions of Reagents** — Prepare the following dilute solutions by diluting the reagent with distilled water.

6.1.2.1 Ammonium hydroxide — 1 : 1 and 1 : 3 (by volume).

6.1.2.2 Ammonium chloride solution — Dissolve 54 g ammonium chloride in one litre distilled water.

6.1.2.3 Ammonium molybdate reagent — Two types of this reagent shall be prepared as follows:

#### 1) Type 1

a) Dissolve 40 g of ammonium molybdate and 20 g of sodium hydroxide in 172 ml of distilled water and filter, and

b) Take 115 ml of 1 : 3 nitric acid.

Mix (a) and (b) and make up the volume to 400 ml (ensure a pH of 1.5 to 1.7) and transfer to plastic bottle for storage.

2) Type 2 — 10 percent solution. Dissolve 10.0 g ammonium molybdate in 80 ml of hot distilled water. Stir till it dissolves. Dilute it to 100 ml with distilled water in 100-ml volumetric flask. Mix and transfer it to a plastic bottle for storage.

6.1.2.4 Ascorbic acid solution — Dissolve 1 g of ascorbic acid in 100 ml of distilled water.

6.1.2.5 Barium chloride solution — Stir 5 g of gelatin and 3 g of polyvinyl alcohol in 50 ml of cold distilled water and add 400 ml of hot distilled water; keep it on water bath for 30 minutes, cool and add 20 g of barium chloride to it. Let the solution stand for 24 hours. Filter through fast filter paper and make up the volume to one litre.

6.1.2.6 Brilliant yellow solution (0.01 percent with stabilizers) — Stir 5 g of polyvinyl alcohol in 50 ml of cold distilled water. After one minute, add 500 ml distilled water and heat the solution on a water bath for 30 minutes; stir

\*Specification for sulphuric acid (second revision).

frequently and cool after complete dissolution. Label this solution as 'I'. Dissolve 0.1000 g of brilliant yellow in 100 ml of distilled water and add this to solution 'I'. Make up the volume to one litre, shake and allow to settle overnight, filter through Whatman filter paper No. 41 and store this solution under refrigeration.

**6.1.2.7 Buffer solution of pH 4.6** — Dissolve 238 g of sodium acetate trihydrate in 500 ml of distilled water and add 102 ml of glacial acetic acid, dilute to one litre with distilled water.

**6.1.2.8 Buffer solution of pH 12.6** — Dissolve 10 g sodium tetraborate and 20 g sodium hydroxide in one litre of distilled water and filter, if required.

**6.1.2.9 Buffer solution of pH 10** — Add 142.5 ml of ammonium hydroxide to 17.5 g of ammonium chloride and dilute to 250 ml with distilled water.

**6.1.2.10 Chromeazurol solution** — Dissolve 0.1650 g of chromeazurol-S in 5 ml of acetone and make up to 1000 ml with distilled water, filter before use.

**6.1.2.11 Dimethyl formamide** — 1 : 9 (by volume).

**6.1.2.12 EDTA solution (0.01 M)** — Dissolve 3.7224 g of EDTA in distilled water and make up to one litre.

**6.1.2.13 Eriochrome black T** — Grind 100 mg of indicator with 10 g of sodium chloride. Store in air-tight polyethylene bottle.

**6.1.2.14 Ferric ammonium sulphate (0.25 M)** — Weigh accurately 3.0116 g of ferric ammonium sulphate, dissolve in 9 N nitric acid and make up to 250 ml with the acid in a volumetric flask.

**6.1.2.15 Ferric nitrate** — Dissolve ferric nitrate in 100 ml water.

**6.1.2.16 Fusion mixture** — Mix carbonates of sodium and potassium in equimolecular proportion.

**6.1.2.17 Glyoxal-bis-2 hydroxyanil solution** — Dissolve 0.7500 g of glyoxal-bis-2 hydroxyanil indicator in 1 litre ethanol.

**6.1.2.18 Hydrochloric acid** — 1 : 1 (by volume).

**6.1.2.19 Hydrogen peroxide** — 6 percent (v/v).

**6.1.2.20 Mercuric thiocyanate solution** — Saturated solution in ethyl alcohol.

**6.1.2.21 Nitric acid** — Sp gr 1.42 (conforming to IS : 264-1976\*); 1 : 1, 1 : 3 (by volume), 9 N and 6 N.

\*Specification for nitric acid (second revision).

#### 6.1.2.22 Reducing agent

a) Dissolve 0.7 g of sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) in 10 ml of distilled water. Add 0.15 g of 1-amino-2-naphthol-4-sulphonic acid. Stir it till it dissolves.

b) Dissolve 9.0 g of sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ) in 80 ml of distilled water in a beaker.

Mix (a) and (b) solutions. Dilute it with distilled water to 100 ml in a volumetric flask. Store it in a dark place. Use this solution for a week only.

**6.1.2.23 Silver nitrate** — Dissolve 0.1575 g of silver nitrate in distilled water and make up to 1 litre in volumetric flask. This will give 100 ppm silver solution.

**6.1.2.24 Sodium hydroxide (2N)** — Dissolve 80 g of sodium hydroxide in distilled water and make up to one litre.

**6.1.2.25 Sodium sulphide** — Dissolve 1.2009 g of sodium sulphide ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) in distilled water, filter and make up to 500 ml in a volumetric flask.

**6.1.2.26 Sodium phosphate solution** — Dissolve 0.1000 g of sodium phosphate solution in one litre of distilled water.

**6.1.2.27 Sulphosalicylic acid solution** — Dissolve 20 g of sulphosalicylic acid in one litre of distilled water.

#### 6.1.2.28 Tartaric acid

a) 1 percent solution — Dissolve 2.5 g of tartaric acid in distilled water and dilute to 250 ml with distilled water.

b) 10 percent solution — Dissolve 10 g of tartaric acid in distilled water and dilute to 100 ml with distilled water.

**6.1.2.29 Triethanolamine solution** — 1 : 9 (by volume).

**6.1.2.30 Triethanolamine + hydroxylamine hydrochloride reagent** — Dissolve 2.5 g of hydroxylamine hydrochloride in 50 ml of distilled water and add 25 ml of triethanolamine and make up to 250 ml.

**6.1.2.31 Zinc solution (0.01 M)** — Dissolve 0.6538 g of pure zinc metal in the minimum quantity of hydrochloric acid and make up to one litre.

**6.1.2.32 Ammonium vanadomolybdate solution** — Dissolve 1 g of ammonium vanadate in 300 ml of distilled water, if possible with the help of mechanical stirring. After complete dissolution, add slowly 140 ml nitric acid (specific gravity 1.42) and 400 ml of 10 percent ammonium molybdate solution. Make up the volume to one

litre with distilled water. Prepare the solution fresh before use.

## 7. DETERMINATION OF MAJOR CONSTITUENTS

**7.1 Decomposition of Test Sample** — Weigh accurately 0.2500 g of test sample in a 20 ml nickel/zirconium crucible and fuse it with approximately 2.5 g of dry sodium hydroxide on a low flame. After the fusion is complete, cool the outer side of the crucible with distilled water. While the melt is still warm, place the crucible on its side in a 500 ml polyethylene beaker, pour 100 ml of boiling distilled water into the beaker and cover it immediately with watch glass. Rinse both the crucible and the lid with distilled water wash both with 5 ml of 5 N hydrochloric acid and then 3 to 4 times with distilled water.

**7.2 Preparation of Stock Solution** — Pour the fusion extract obtained in 7.1 through a polyethylene funnel into a 500-ml volumetric flask containing 50 ml of 5 N hydrochloric acid. Swirl the flask rapidly to obtain a clear solution. Take care to obtain a clear solution.

In case any turbidity appears due to colloidal silica, reject the solution and start afresh with fusion. The solution of acidified fusion extract thus obtained contains monomeric  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  and it has a pH of approximately 1 to 1.5; the pH may, however, be checked to ensure that it is in the range of 1 to 1.5. Label this as stock solution A.

**7.2.1** Alternatively, weigh accurately 0.2500 g of test sample in a platinum crucible, add 2.5 g of sodium carbonate and 1.0 g of boric acid. Mix well. Heat the crucible on a low flame for about ten minutes and then at 1000°C in a muffle furnace for about 20 minutes. After fusion is complete, cool the outside of the crucible with distilled water. While the melt is still warm, place the crucible on its sides in 250 ml beaker containing 17.5 ml of concentrated nitric acid and 100 ml distilled water. Transfer the solution in a 500 ml volumetric flask and dilute it to the mark with distilled water. Label this as stock solution B.

### 7.3 Preparation of Blank Solution

**7.3.1 For Stock Solution A** — Dissolve 2.5 g of dry sodium hydroxide in distilled water, add 55 ml of 5 N HCl, transfer the solution to a 500 ml flask and dilute to the mark with distilled water. Label this solution as C. This solution is used subsequently for the preparation of reagent blank along with stock solution A.

**7.3.2 For Stock Solution B** — Dissolve 2.5 g of sodium carbonate and 1.0 g of boric acid in 10.5 ml concentrated nitric acid. Transfer this solution in 500 ml volumetric flask and dilute to the mark with distilled water. Label the solution as D. This solution is used subsequently for the preparation of reagent blank along with stock solution B.

## 7.4 Silica

### 7.4.1 Method 1

**7.4.1.1 Outline of the method** — With ammonium molybdate, monomeric silica forms a stable yellow silico-molybdic complex under controlled conditions of pH, 1.7 — 3.7, in aqueous ethanol medium. Phosphorus, arsenic and germanium interfere with the estimation. Interference due to phosphorus is eliminated by using organic acids like tartaric or citric acid. Arsenic and germanium can be completely volatilized by boiling with hydrochloric acid. The optical density of the test solution (from which the interfering agents have been removed) is measured at 410 m $\mu$  after a total of 15 $\pm$ 2 minutes of colour generation at 32 $\pm$ 1°C.

**7.4.1.2 Preparation of standard stock solution** — Weigh 0.1000 g of pure ground quartz passing through 106  $\mu\text{m}$  IS Sieve in a nickel/zirconium crucible. Add 1.5 g of sodium hydroxide pellets to it, cover the crucible and heat on a medium mecker flame to dull red for 5 to 7 minutes. Heat it further for 2 to 3 minutes if the fusion is not complete, cool and extract with 100 ml of boiling distilled water in polyethylene beaker. Add to the extract, 12 ml of 5 N hydrochloric acid to yield a clear solution. Make up to the mark in a 500 ml volumetric flask with distilled water. The stock solution thus obtained will have a concentration of 200 ppm  $\text{SiO}_2$ .

**NOTE** — Alternatively, prepare standard stock solution using National Council for Cement and Building Materials/National Bureau of Standards chemically analyzed standard reference cement samples, and suitable aliquots may be taken for calibration.

**7.4.1.3 Calibration** — Pipette out 1, 3, 5, 7, 9, 10, 12, 14, 16, 18 and 20 ml of the 200 ppm  $\text{SiO}_2$  solution into eleven different 100 ml volumetric flasks. Add 19, 17, 15, 13, 11, 10, 8, 6, 4, 2 and 0 ml of blank for stock solution A (see 7.3.1). Then add the following in the sequence indicated to each of the flasks and make up to 100 ml with distilled water:

- a) 5 ml tartaric acid,
- b) Water to bring up the volume to about 80 ml,
- c) 5 ml acetone, and
- d) 10 ml ammonium molybdate reagent.

Prepare a blank solution with 20 ml blank solution for stock solution A, adding the reagents mentioned in the same order. Immerse the flasks exactly for 10 minutes in a water bath maintained at 32 $\pm$ 1°C. Pour each of the solution immediately on preparation into an absorption cell and measure the respective optical densities at 410 m $\mu$  after a total of 15 $\pm$ 2 minutes of colour generation against reagent blank. Read optical density value up to 7 ppm  $\text{SiO}_2$  directly against blank and

let this value be  $x$ . Then adjust this to zero in order to expand the scale of observation. If the optical density reading for a solution is now  $y$ , then its optical density against blank will be  $x+y$ .

Draw the calibration curve by plotting different values of optical density against the respective concentrations in ppm of silica. Whenever any fresh reagent solution is prepared, the calibration should be checked for correctness and redrawn, if necessary.

**7.4.1.4 Estimation in test solution** — Take 15 to 25 ml aliquot of stock solution *A*, the acidified fusion extract, in a 100 ml volumetric flask and add all the reagents in the same sequence as in 7.4.1.3. Make up the volume to 100 ml and measure the optical density exactly as done for the calibration. From the value of the optical density, read out the concentration of silica from the calibration curve. Calculate the percentage of silica as follows:

Silica, percent

$$= \frac{\text{Concentration in ppm (from graph)} \times 20}{\text{Volume of aliquot}}$$

## 7.4.2 Method 2

**7.4.2.1 Outline of the method** — Silicon forms an intense yellow coloured complex with ammonium molybdate under acidic conditions. The silico-molybdic acid is reduced to molybdenum blue by reducing agent. Phosphorus, arsenic and germanium interfere with the estimation. Interference due to phosphorus is eliminated by using organic acids like tartaric, citric or oxalic acid. Arsenic and germanium, if present, can be completely volatilized by boiling with hydrochloric acid. The optical density of the test solution (from which the interfering agents have been eliminated) is measured at 650  $m\mu$  after a total of 15 minutes of colour generation.

**7.4.2.2 Preparation of standard stock solution** — Weigh 0.1000 g of pure quartz passing through 106  $\mu\text{m}$  IS Sieve in a platinum crucible. Take 2.5 g of sodium carbonate and 1.0 g of boric acid and transfer it to crucible containing the sample. Mix intimately with platinum rod or teflon rod. Cover it with platinum lid. Heat the crucible on a low flame for about 10 minutes and then at 1000°C for about 20 minutes. After the fusion is complete, cool the outside of the crucible with distilled water. While the melt is still warm, place the crucible on its sides in 250 ml beaker containing 17.5 ml concentrated nitric acid and 100 ml distilled water. Transfer the solution in a 1000 ml volumetric flask and dilute it to the mark with distilled water. The stock solution thus obtained will have a concentration of 100 ppm  $\text{SiO}_2$ .

NOTE — Alternatively, prepare standard stock solution from NBS\*/NCB† chemically analysed SRM

\*NBS — National Bureau of Standards.

†NCB — National Council for Cement and Building Materials.

cement samples and suitable aliquots may be taken for calibration.

**7.4.2.3 Calibration** — Pipette out 1, 2, 3, 4, 5 and 6 ml of 100 ppm  $\text{SiO}_2$  solution into different 100 ml volumetric flasks. Add 2.5, 2, 1.5, 1, 0.5 and 0 ml of blank solution for stock solution *B* (see 7.3.2) to above flasks (for example, in a flask containing 1 ml of aliquot solution, add 2.5 ml of blank solution and similarly for 3 ml aliquot, add 1.5 ml of blank solution and so on). Dilute it approximately to 70 ml with distilled water. Add the following in the sequence indicated to each of the flasks and make up to 100 ml with distilled water:

- 5 ml of 10 percent ammonium molybdate solution (see 6.1.2.3, Type 2). Mix well and allow to stand for 5 minutes;
- 5 ml of tartaric acid;
- 3 ml of concentrated nitric acid and mix well; and
- 5 ml of reducing agent and mix well.

Prepare a blank solution using 5 ml of blank solution for stock solution *B* adding the reagents mentioned in the same order. Allow the solution to stand for about 15 minutes. Pour each of the solution into an absorption cell and measure the respective optical densities against the reagent blank at 650  $m\mu$ .

Draw the calibration curve by plotting the values of optical density against respective concentration in ppm of silica. Whenever any fresh reagent solution is prepared, the calibration should be checked for correctness and redrawn, if necessary.

**7.4.2.4 Estimation in test solution** — Take 2.5 ml aliquot from stock solution *B* in a 100 ml volumetric flask and add 2.5 ml of blank solution for stock solution *B*. Add all the reagents in the same sequence as in 7.4.2.3. Make up the volume to 100 ml and measure the optical density against reagent blank exactly as done for the calibration. From the value of the optical density, read out the concentration of silica from the calibration curve. Calculate the percentage of silica as follows:

Silica, percent

$$= \frac{\text{Concentration in ppm (from graph)} \times 20}{\text{Volume of aliquot}}$$

## 7.5 Alumina

**7.5.1 Outline of the Method** — Aluminium forms a stable complex with chromeazurols-S at pH 4.6. The sesquioxide of iron and titanium interfere with the estimation but are masked by complexing with ascorbic acid and sodium phosphate, respectively. The simultaneous presence of silica and manganese as well as large quantities of calcium do not disturb the estimation. The

optical density of the solution is measured at 568 m $\mu$ .

**7.5.2 Preparation of Standard Stock Solution** — Dissolve 0.5292 g of pure aluminium metal in 10 ml 1:1 hydrochloric acid, heat the contents to complete dissolution and cool. Make up to one litre with distilled water in order to get a solution of 1 000 ppm alumina and label it *E*. Take 10 ml of *E* and make up to one litre with distilled water in order to get a solution of 10 ppm alumina and label it *F*.

NOTE — Alternatively, prepare stock solution using National Council for Cement and Building Materials/ National Bureau of Standards standard reference cement samples, and suitable aliquots may be taken for calibration.

**7.5.3 Calibration** — Pipette out, in a series of 100-ml volumetric flasks, 0.5, 1, 2, 4, 6 and 9 ml of solution *F* and add the following reagents in the sequence indicated and proceed as under:

- 2 ml ascorbic acid solution,
- 5 ml of sodium phosphate solution. Leave for 5 minutes in contact and dilute with 50 ml of distilled water. Then add:
- 5 ml of buffer solution of pH 4.6, and
- 20 ml of chromeazurole-S (accurately measured).

Prepare a reagent blank exactly in the same manner starting with distilled water. Leave in contact for 15 minutes and make up the volume to 100 ml with distilled water. Measure the optical density using a 10 mm thick cell at 568 m $\mu$ . The net optical density is obtained by subtracting reagent blank from the measured optical density.

Draw the calibration curve by plotting different values of net optical density against the respective concentrations in ppm of alumina. Whenever fresh reagent solutions are prepared, check the calibration curve with two or three points and adjust the curve, if necessary. Since the complexing agent chromeazurole-S is highly coloured, it is desirable to carry out a fresh calibration (3 points are sufficient) from one series of measurements to another.

NOTE — Use suitable aliquots of blank solution for stock solution *A* or blank solution for stock solution *B* when standard stock solution is made from cement sample.

**7.5.4 Estimation in Test Solution** — Dilute 10 ml of stock solution *A* or *B* to 100 ml. Take 5 to 25 ml aliquot of this solution (containing 0.01 mg to 0.09 mg of Al<sub>2</sub>O<sub>3</sub>) in a 100-ml volumetric flask and add all the reagents in the same sequence as in 7.5.3. Make up the volume to 100 ml and measure the optical density exactly as done for the calibration. From the value of the net optical density, read out the concentration

of alumina from the calibration curve. Calculate the percentage of alumina as follows:

$$\text{Alumina, percent} = \frac{\text{Concentration in ppm (from graph)} \times 200}{\text{Volume of aliquot}}$$

NOTE — If the test solution is highly acidic, neutralize it partially with 10 percent NaOH using methyl orange indicator; this is not required with slightly acidic solution.

## 7.6 Iron Oxide

**7.6.1 Outline of the Method** — Iron forms a yellow complex with sulphosalicylic acid in ammoniacal medium. Iron can be determined in the presence of up to five times its weight of titanium or cobalt. Silicon, aluminium, calcium, magnesium, sodium, potassium and lithium do not interfere. The optical density of the solution is measured at 420 m $\mu$ .

**7.6.2 Preparation of Standard Stock Solution** — Dissolve 0.6994 g of pure iron powder or 6.0397 g of ferric alum [Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·24H<sub>2</sub>O] in the minimum quantity of concentrated hydrochloric acid. Add a few drops of concentrated nitric acid and boil. After dissolution is complete, make up the volume to one litre with distilled water. The stock solution thus obtained will have a concentration of 1 000 ppm ferric oxide. Take 100 ml of the stock solution and make up to one litre with distilled water in order to get a solution of 100 ppm ferric oxide.

NOTE — Alternatively, standard stock solution obtained from NBS/NCB chemically analysed SRM cement samples may be used for calibration with suitable aliquots.

**7.6.3 Calibration** — Pipette out 2, 4, 6, 8, 10, 12 and 16 ml of 100 ppm ferric oxide solution into eight different volumetric flasks, each of 100 ml capacity. Then add the following reagents in the sequence indicated:

- 5 ml ammonium chloride, and
- 6 ml sulphosalicylic acid solution (10 ml in case of PPC).

Add ammonia solution till the pink colour of the original solution changes to bright yellow, add 1 ml more of ammonia solution and make the volume to 100 ml with distilled water. Prepare a blank solution with distilled water, adding these reagents mentioned in the same order. Measure the optical density of each of the above eight solutions at 420 m $\mu$  against the blank using a 10 mm cell. Draw the calibration curve by plotting different values of optical density against the respective concentrations in ppm of ferric oxide. It is necessary to check the calibration curve from time to time.

NOTE — Use suitable aliquots of blank solution for stock solution *A* or blank solution for stock solution *B* when standard stock solution is made from cement sample.

**7.6.4 Estimation in Test Solution** — Take 10 to 15 ml aliquot of stock solution *A* or *B* in a 100-ml volumetric flask. Add the two reagents in the sequence mentioned in 7.6.3. Make up the volume to 100 ml with distilled water and measure the optical density at 420 m $\mu$  exactly as done for the calibration. From the value of the net optical density, read out the concentration of ferric oxide from the calibration curve. Calculate the percentage of ferric oxide as follows:

Ferric oxide, percent

$$= \frac{\text{Concentration in ppm (from graph)} \times 20}{\text{Volume of aliquot}}$$

## 7.7 Calcium Oxide

**7.7.1 Outline of the Method** — Glyoxal-bis-2 hydroxyanil forms a 1 : 1 red coloured complex with calcium at pH 12.6. Since the colour of the complex is highly susceptible to time, the optical density is measured within 2 to 4 minutes of addition of the indicator. Though the colour generation is highly specific and reproducible, yet it is not possible to estimate calcium up to 70 percent by the normal procedure. Hence a combination of complexometry and colorimetry has been adopted. The complexometric part consists in the addition of a calculated amount of EDTA to the test solution so that some calcium, not exceeding 10 percent, is left uncomplexed in the solution. The mixture is then analysed colorimetrically at 570 m $\mu$ . Iron interferes with the estimation but is masked by the addition of triethanolamine.

**7.7.2 Preparation of Standard Stock Solution** — Dissolve 1.7857 g of pure calcium carbonate in the minimum quantity of hydrochloric acid. After dissolution is complete, make up the volume to one litre with distilled water. The stock solution thus obtained will have a concentration of 1 000 ppm calcium oxide.

NOTE — Alternatively, standard stock solution obtained from NBS/NCB chemically analysed SRM cement samples may be used for calibration with suitable aliquots.

**7.7.3 Standardization of EDTA** — Dilute 25 ml of the standard zinc solution (0.01 M) to 100 ml with distilled water, add 20 ml of the buffer solution of pH 10 and 50 mg of Eriochrome Black T indicator. Titrate with EDTA solution until the colour changes from wine red to blue.

1 ml 0.01 M EDTA  $\equiv$  0.6538 mg zinc.

**7.7.4 Calibration** — Pipette out 25 ml of the standard stock solution of 1 000 ppm calcium oxide in a 250-ml volumetric flask and add to it 22.90 ml of 0.01 M EDTA solution and make up the volume. Since 1 ml of 0.01 M EDTA  $\equiv$  0.5608 mg of calcium oxide, the solution will now correspond to 50 ppm calcium oxide. Pipette out 2, 4, 6, 8, 10 and 12 ml of this solution into different 100-ml volumetric flasks. Then add the

following to each of the flask in the sequence indicated:

- 10 ml triethanolamine,
- 20 ml buffer solution of pH 12.6, and
- 40 ml glyoxal-bis-2-hydroxyanil reagent.

Make up the volume to 100 ml in each case with distilled water. Prepare a blank solution with distilled water, adding the reagents mentioned in the same order. Measure the optical density of each of the above solutions at 570 m $\mu$  against water using a 10 mm cell. The net optical density of the solutions is obtained by subtracting the reagent blank. Draw the calibration curve by plotting different values of net optical density against the respective concentrations in ppm calcium oxide. It is desirable to check the calibration curve from time to time.

NOTE — Use suitable aliquots of blank solution for stock solution *A* or blank solution for stock solution *B* when standard stock solution is made from cement sample.

**7.7.5 Estimation of Test Solution** — Pipette out 50 ml of stock solution *A* or *B*, in a 100-ml volumetric flask and to this, add 25.85 ml of 0.01 M EDTA solution (equivalent to 58 percent calcium oxide) and make up the volume (see Notes 1 and 2). Label this as solution *G*. Pipette out 5 to 20 ml aliquot from *G* into 100-ml flask and add all the reagents in the same sequence as mentioned under 7.7.4. Make up the volume to 100 ml with distilled water and measure the optical density, read out the concentration of CaO equivalent to available lime after EDTA complexation. To this percentage of lime, now add percentage of lime equivalent to which EDTA has been added. Calculate the percentage of calcium oxide as follows:

$$\text{Calcium oxide, percent} = \frac{\text{Concentration in ppm (from graph)} \times 40}{\text{Volume of aliquot}} + 58$$

NOTE 1 — In case of Portland pozzolana cement, add 20.05 ml of 0.01 M EDTA (equivalent to 45 percent calcium oxide).

NOTE 2 — In case of Portland slag cement, add 15.60 ml of 0.01 M EDTA (equivalent to 35 percent calcium oxide).

## 7.8 Magnesia

**7.8.1 Outline of the Method** — With Brilliant Yellow (the sodium salt of 2,2'-disulphostilbene 4,4'-diazobisphenol), magnesium forms a scarlet lake in alkaline medium. Although, the colloidal suspensions are fairly stable, say, up to 10 minutes but the optical density of the test solution should preferably be measured after 1 to 2 minutes of adding the reagent. The measurement is made at 550 m $\mu$ . The main interference is from dissolved silica and manganese. Silica up to 30 percent is masked by dimethyl formamide while the interference from manganese is overcome by



using reducing agents like hydroxylamine hydrochloride. Interference due to iron, aluminium and calcium is overcome by incorporating them in the same amounts in sample and standards.

**7.8.2 Preparation of Standard Stock Solution** — Dissolve 6.115 g of pure hydrated magnesium sulphate [ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ] in distilled water. After dissolution is complete, make up the volume to one litre. The stock solution thus obtained will have a concentration of 100 ppm magnesia.

**NOTE** — Alternatively, standard stock solution obtained from NBS/NCB chemically analysed SRM cement samples may be used for calibration with suitable aliquots.

**7.8.3 Preparation of Composite Solution** — Dispense suitable volumes of silica, alumina, ferric oxide, calcium oxide and magnesia solutions in a 500-ml volumetric flask as to give a composite solution of 100 ppm silica, 325 ppm calcium oxide, 30 ppm alumina, 25 ppm ferric oxide and 20 ppm magnesia and make up with distilled water.

**7.8.4 Calibration** — Pipette out 2.5, 5, 10, 20, 25 and 30 ml of 20 ppm MgO composite solution into different 100-ml volumetric flasks. Add the following in the given order, mixing well after each addition but avoiding bubbles by swirling gently in one direction only:

- 10 ml triethanolamine hydroxylamine hydrochloride mixture (see Note 2),
- About 40 ml distilled water,
- 5 ml dimethyl formamide,
- 10 ml Brilliant Yellow reagent, and
- 10 ml of 2 N sodium hydroxide.

After making up the volume with distilled water, mix thoroughly and measure optical density of each of the solutions at 550  $m\mu$  within two minutes of colour generation against distilled water, using a 10 mm cell. Prepare a reagent blank with distilled water adding the reagents mentioned in the same order. The net optical density is obtained by subtracting the reagent blank from the measured optical density. Draw the calibration curve by plotting the different values of net optical density against the respective concentrations in ppm of MgO. It is desirable to check the calibration curve from time to time.

**NOTE 1** — Use suitable aliquots of blank solution for stock solution A or blank solution for stock solution B when standard stock solution is made from cement sample.

**NOTE 2** — When samples contain more than 0.2 percent  $\text{Mn}_2\text{O}_3$ , the quantity of the reagent should be increased to overcome interference due to  $\text{Mn}_2\text{O}_3$ .

**7.8.5 Estimation in Test Solution** — Transfer 5 to 20 ml of stock solution A or B into a 100-ml volumetric flask and add all the reagents in

the same sequence as given in 7.8.4. Make up the volume to 100 ml with distilled water and measure the optical density exactly as done for the calibration. The net optical density is obtained by subtracting the reagent blank from the optical density. From the value of the net optical density, read out the concentration of MgO. Calculate the percentage of magnesia as follows:

$$\text{Percent MgO in the sample} = \frac{\text{Concentration in ppm (from graph)} \times 20}{\text{Volume of aliquot}}$$

## 7.9 Sulphuric Anhydride

**7.9.1 Outline of the Method** — Sulphate is determined by turbidimetric technique by adding barium chloride solution (stabilised) to the test solution at pH 1.5 to 2.5. Silica interferes due to its tendency of getting co-precipitated with barium sulphate. This is overcome by the addition of dimethyl formamide solution. The optical density is measured at 502  $m\mu$ .

**7.9.2 Preparation of Standard Stock Solution** — Dissolve 2.1775 g of dry potassium sulphate in distilled water and make up to one litre. This solution contains 1 000 ppm sulphate.

**NOTE** — Alternatively, standard stock solution obtained from NBS/NCB chemically analysed SRM cement samples may be used for calibration with suitable aliquots.

**7.9.3 Preparation of Standard Stock Solution with Calcium Oxide as Compensator** — Measure out 100 ml of the stock solution under 7.9.2 in a one litre measuring flask and add 3.5714 g of pure calcium carbonate in it. Dissolve by shaking and addition of dilute hydrochloric acid till a clear solution is obtained. Make up the volume with distilled water.

**7.9.4 Preparation of Silica Solution** — Weigh 0.125 g of pure quartz in a nickel/zirconium crucible and proceed for the preparation of silica solution as under 7.4.1.2. Make up the volume to 250 ml. The stock solution thus obtained has a concentration of 500 ppm silica.

**7.9.5 Calibration** — Pipette out 2.5, 5, 7.5, 12.5, 17.5 and 20 ml of solution under 7.9.3 and 2 times these volumes of solution under 7.9.4 into different 100-ml volumetric flasks. Add the following reagents in the sequence indicated:

- 10 ml dimethyl formamide, and
- 15 ml stabilized barium chloride solution.

Make up the volume to 100 ml in each case with distilled water. Measure the optical density of each of the above solutions at 502  $m\mu$  using a 10 mm absorption cell after 5 minutes of adding the barium chloride solution. Prepare a blank solution with distilled water, adding the reagents mentioned in the same order. The net optical density is obtained by subtracting the reagent

blank from the measured optical density. Draw the calibration curve by plotting the different values of optical density against the respective concentrations in ppm of sulphate. Whenever a fresh reagent is prepared, check the calibration with two or three standards and adjust the curve if necessary. Also, wash the absorption cell with EDTA solution after each measurement since barium sulphate has a tendency to adhere to the walls of the cell.

**NOTE** — Use suitable aliquots of blank solution for stock solution *A* or blank solution for stock solution *B* when standard stock solution is made from cement sample.

**7.9.6 Estimation in Test Solution** — Take 20 to 25 ml aliquot of stock solution *A* or *B* in a 100-ml volumetric flask, and add all the reagents in the same sequence as mentioned under 7.9.5. Make up the volume to 100 ml with distilled water and measure the optical density at 502 m $\mu$  using a 10 mm absorption cell exactly as done for the calibration. From the value of the net optical density, read out the concentration of sulphate from the calibration curve. Calculate the percentage of sulphuric anhydride as follows:

Sulphuric anhydride, percent

$$= \frac{\text{Concentration in ppm (from graph)} \times 20}{\text{Volume of aliquot}}$$

## 8. DETERMINATION OF MINOR CONSTITUENTS

### 8.1 Titanium Dioxide

**8.1.1 Outline of the Method** — Ti<sup>4+</sup> forms a yellow complex with hydrogen peroxide in acid medium, the most suitable acid for this purpose being sulphuric acid of 2N to 3N concentration. Iron interferes with the estimation but is masked by using phosphoric acid. Calcium and magnesium do not affect the estimation. The optical density is measured at 410 m $\mu$ .

**8.1.2 Preparation of Standard Stock Solution** — Boil a mixture of 0.4433 g of potassium titanium oxalate [K<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O], 1 g of ammonium sulphate and 25 ml of concentrated sulphuric acid for 15 minutes. Cool and dilute to 1 litre with distilled water to get a 100 ppm titanium dioxide solution.

**8.1.3 Calibration** — Pipette 2, 5, 8, 10, 15 and 20 ml of 100 ppm titanium dioxide solution into different 100-ml volumetric flasks. Add the following in the sequence indicated:

- 5 ml phosphoric acid (1 : 3), and
- 5 ml of 6 percent hydrogen peroxide.

Make up the volume to 100 ml with distilled water. Prepare blank solution under identical conditions. Measure the optical density of each of the solutions against the reagent blank at 410 m $\mu$ . Draw the calibration curve by plotting

the optical density against the respective concentrations in ppm of titanium dioxide.

**8.1.4 Preparation of Test Solution and Estimation** — Treat 1 g of the sample with 20 ml of concentrated hydrochloric acid, boil, dilute with hot distilled water and filter off silica; preserve the filtrate. Fuse the residue left after hydrofluorization of silica with 1 : 1 borax and sodium carbonate mixture and dissolve in hydrochloric acid. Add the solution of filtrate obtained after removing silica and then precipitate R<sub>2</sub>O<sub>3</sub> by adding two or three drops of methyl red solution and 1 g of ammonium chloride and precipitate the hydroxides by adding 1 : 2 ammonia solution drop by drop till the solution turns yellow. Stir vigorously during the precipitation. Filter off the precipitate of R<sub>2</sub>O<sub>3</sub>, wash first with distilled water and then with hot 1 : 3 H<sub>2</sub>SO<sub>4</sub> and collect the washings in a 100-ml volumetric flask. Finally wash the filter paper with hot water till the volume reaches about 85 ml, cool and add all the reagents in the same sequence as mentioned in 8.1.3. Make up the volume to 100 ml with distilled water. Shake the contents of the flask thoroughly and measure the optical density at 410 m $\mu$  against the reagent blank and read the titanium dioxide concentration in ppm from the calibration curve. Calculate the percent of titanium dioxide as follows:

Titanium dioxide, percent

$$= \frac{\text{Concentration in ppm (from graph)}}{100}$$

### 8.2 Manganese Oxide

**8.2.1 Outline of the Method** — Manganese is oxidized to permanganate by the action of potassium periodate in nitric acid solution. Iron and chloride interfere with the estimation. Interference of chloride is overcome by evaporating the solution with sulphuric acid and that of iron by using phosphoric acid. The optical density is measured at 525 m $\mu$ .

**8.2.2 Preparation of Standard Stock Solution** — Dissolve 0.6959 g of pure manganese powder in 15 ml of concentrated nitric acid. If pure manganese is not available, prepare the solution from potassium permanganate. Generate the colour by adding 1 g of potassium periodate followed by heating the solution on water bath for about 30 minutes. Make up volume to 1 litre with distilled water. This will give a 1000 ppm manganese oxide solution.

**8.2.3 Calibration** — Dilute 25 ml of 1000 ppm manganese oxide solution to 500 ml to get 50 ppm manganese oxide solution. Pipette out 2, 5, 7, 9, 11, 13 and 15 ml of this solution into different 50-ml volumetric flasks. Add 5 ml of 1 : 3 phosphoric acid and make up the volume with distilled water. Prepare reagent blank with distilled water under identical conditions.

Measure the optical density of the above solutions at  $525\text{ m}\mu$  against reagent blank using 10 mm cell. Draw the calibration curve by plotting different values of optical density against the respective concentrations in ppm of manganese oxide.

**8.2.4 Preparation of Test Solution and Estimation** — Treat 1 g of the sample with 10 ml of concentrated nitric acid, heat for 5 minutes, dilute with hot water and filter off. Collect the filtrate in a 100-ml beaker and add to it, 0.5 g of potassium periodate and keep the beaker on a water bath for about 45 minutes. After the colour is developed, cool the beaker and then transfer the solution to a 50-ml volumetric flask taking care to wash down all the contents to the volumetric flask with distilled water. Add 5 ml 1 : 3 phosphoric acid and make up the volume with distilled water. Measure the optical density at  $525\text{ m}\mu$  against the reagent blank and read the concentration of manganese oxide from the calibration curve. Calculate the percent of manganese oxide as follows:

$$\text{Manganese oxide, percent} = \frac{\text{Concentration in ppm (from graph)}}{200}$$

### 8.3 Phosphorus Pentoxide

**8.3.1 Outline of the Method** — Phosphorus on treatment with ammonium vanadomolybdate, gives a yellow coloured ammonium phosphovanadomolybdate complex. This yellow coloured complex is extracted with amyl alcohol to avoid interference by silica and iron. The optical density is measured at  $426\text{ m}\mu$ .

**8.3.2 Preparation of Standard Stock Solution** — Weigh exactly 0.1860 g of dry diammonium hydrogen orthophosphate  $[(\text{NH}_4)_2\text{HPO}_4]$ , dissolve in distilled water and make up to 500 ml. This will give a 200 ppm phosphorus pentoxide solution.

**8.3.3 Calibration** — Pipette out 0.5, 1, 2, 3, 4, 5, 6.5, 8, 9 and 10 ml of the 200 ppm phosphorus pentoxide solution into 100-ml volumetric flasks, add 25 ml of ammonium vanadomolybdate solution to each, shake and make up the volume. These will correspond to 1, 2, 4, 6, 8, 10, 13, 16, 18 and 20 ppm phosphorus pentoxide solutions. Run 10 ml amyl alcohol (exactly measured) into a 150-ml conical separating funnel, then add 1 ppm phosphorus pentoxide solution from the first volumetric flask. Shake the contents of the separating funnel vigorously for 2 minutes and allow to settle for 5 minutes. Run off the aqueous layer completely. Run off about 1 ml of alcoholic layer in order to rinse the stem of the separating funnel and filter the remainder of the extract through a small Whatman No. 40 filter paper. Discard the first few drops of the filtrate and collect finally the clear amyl alcohol extract in a 10 mm absorption cell. Repeat the process for

the other solutions also and measure the optical density against the reagent blank (prepared in the same manner starting with distilled water) at  $426\text{ m}\mu$ . Draw the calibration curve by plotting the different values of optical density against the respective concentrations in ppm of phosphorus pentoxide.

**8.3.4 Preparation of Test Solution and Estimation** — Weigh 0.2 g of the sample into a 100-ml beaker, add 1 ml of water and 1 ml of concentrated nitric acid (sp gr 1.42). Stir and add 5 ml of 60 percent perchloric acid. Cover the beaker with a watch glass and warm on a hot plate in a fume chamber. Adjust the temperature so that thick white fumes of perchloric acid appear after 3 minutes. Then move the beaker to the cooler part of the hot plate and continue the reaction for 10 minutes, allowing to fume gently. Remove the beaker from the hot plate and cool. Add 20 ml of water, filter through a Whatman No. 40 filter paper into a 300-ml conical flask and wash four times with hot water. Heat the filtrate to just below the boiling point, cool and transfer into 100-ml volumetric flask. Add 25 ml of ammonium vanadomolybdate solution, make up the volume by adding distilled water, shake and keep for about 2 minutes. Proceed exactly as in the calibration and measure the optical density at  $426\text{ m}\mu$ . A blank determination is absolutely necessary as amyl alcohol extracts faint colour from the ammonium vanadomolybdate solution. From the net optical density value, the concentration of phosphorus pentoxide is read from the calibration curve. Calculate the percent of phosphorus pentoxide as follows:

$$\text{Phosphorus pentoxide, percent} = \frac{\text{Concentration in ppm (from graph)}}{20}$$

### 8.4 Chloride

#### 8.4.1 Method 1

**8.4.1.1 Outline of the method** — Chloride ions displace thiocyanate ions from mercuric thiocyanate; in the presence of ferric ion, a highly coloured ferric thiocyanate complex is formed, the intensity of which is proportional to the original chloride ion concentration. The optical density is measured at  $460\text{ m}\mu$ .

**8.4.1.2 Preparation of stock solution** — Dry potassium chloride at  $110^\circ\text{C}$  for about 2 hours. Dissolve 2.0986 g of the salt in distilled water and make up to one litre. This solution provides a concentration of 1000 ppm chloride. Take 50 ml of this solution and make up to one litre in order to get a stock solution of 50 ppm chloride.

**8.4.1.3 Preparation of blank solution** — Measure appropriate volumes of solutions  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  in a 500-ml volumetric

flask so as to provide a composite solution of 15 000 ppm CaO, 875 ppm Fe<sub>2</sub>O<sub>3</sub>, 15 00 ppm Al<sub>2</sub>O<sub>3</sub>, and 500 ppm MgO.

**8.4.1.4 Calibration** — Pipette out 2, 4, 6, 8 and 10 ml of stock solution under 8.4.1.2 into different 100-ml volumetric flasks. Add 20 ml of blank solution under 8.4.1.3 to each of the flasks. Add the following reagents in the sequence indicated:

- a) 10 ml saturated solution of mercuric thiocyanate in ethyl alcohol, and
- b) 5 ml ferric nitrate.

Make up the volume to 100 ml with distilled water. Prepare a reagent blank solution adding the reagents under identical conditions including 20 ml blank solution under 8.4.1.3. Measure the optical density of the above solutions after 5 minutes at 460 m $\mu$  against reagent blank. Draw the calibration curve by plotting the different values of net optical density against the respective concentration in ppm of chloride.

**8.4.1.5 Preparation of test solution and estimation** — Weigh accurately 0.50 g of test sample in a beaker, moisten with water and add 10 ml of HNO<sub>3</sub> (1 : 1), heat to boil to ensure complete decomposition. Filter through Whatman No. 40 filter paper into 100-ml flask. Add the following in the sequence indicated:

- a) 10 ml saturated solution of mercuric thiocyanate, and
- b) 5 ml ferric nitrate.

Make up the volume to the mark. Measure the optical density against the reagent blank at 460 m $\mu$  after 5 minutes. Calculate the percentage of chloride as follows:

Chloride, percent =

$$\frac{\text{Concentration in ppm (from graph)}}{50}$$

## 8.4.2 Method 2

**8.4.2.1 Outline of the method** — Estimation of chloride is based on the precipitation of chloride by silver nitrate as silver chloride and dissolving the precipitate in ammonia. Brownish yellow coloured solution of silver sulphide is obtained by adding sodium sulphide to the ammoniacal solution and measuring the silver content. The chloride content is obtained by multiplying the silver content by 0.329.

**8.4.2.2 Preparation of standard stock solution** — Weigh exactly 0.157 51 g of silver nitrate and dissolve in distilled water and make up to 1 litre in a volumetric flask. This will give a 100 ppm silver solution.

**8.4.2.3 Calibration** — Pipette out 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml of silver solution in different 100-ml volumetric flasks. These will be 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ppm of silver solution, respectively. Add 3 ml of 1 : 1 NH<sub>4</sub>OH solution to each flask, make the volume to about 90 ml with distilled water and then add 2 ml of 0.01 M sodium sulphide in each flask and make the volume to 100 ml in each case. Prepare a blank solution by adding likewise amount of each solution except the silver solution. Measure the optical density of each solution against the reagent blank at 415 m $\mu$  after 5 minutes of making up the volume. Draw a standard calibration curve between silver concentration and optical density.

**8.4.2.4 Preparation of test solution and estimation** — Weigh exactly 0.5 g of the sample (see Note) and dissolve in the minimum quantity of 1 : 1 HNO<sub>3</sub>, dilute with distilled water to 50 ml. Heat for about 5 minutes and filter through Whatman No. 40 filter paper into a 100-ml volumetric flask. Add 10 ml or more of 100 ppm silver solution to the filtrate to ensure complete precipitation and digest the silver chloride precipitate on a water bath for 3 hours. Filter through Whatman No. 42 filter paper and wash twice with hot water. Discard the filtrate. Dissolve the precipitate in 3 ml of 1 : 1 NH<sub>4</sub>OH. Transfer the contents in a 100-ml volumetric flask. Dilute to about 90 ml with distilled water and add 2 ml of 0.01 M sodium sulphide and make up the volume. Measure optical density after 5 minutes at 415 m $\mu$ . Corresponding to the optical density of unknown cement solution obtained above, get the silver concentration from the standard calibration curve. Multiply the silver concentration by 0.329 to get the chloride concentration in ppm in that particular volume. Chloride percentage in the sample shall be calculated as follows:

Chloride, percent

$$= \frac{\text{Concentration in ppm of chloride}}{50}$$

NOTE — The mass of sample shall be 1.5 to 2 g in cases where chloride content is 0.01 percent.

**PRINTED AT SIMCO PRINTING PRESS, DELHI (INDIA)**

BE  
ONLY