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भारतीय मानक मसौदा

कोयले और कोक – राख के रासायनिक संघटन का निर्धारण करने की विधियाँ

(आईएस 1355 का दूसरा पुनरीक्षण)

Draft Indian Standard

**COAL AND COKE — METHODS OF DETERMINATION OF THE CHEMICAL
COMPOSITION OF ASH**

(Second Revision of IS 1355)

(ICS 73.040, 75.160.10)

Solid Mineral Fuels and Solid Biofuels
Sectional Committee, PCD 07

Last date for Comments:
12 July 2024

FOREWORD

(Formal clauses will be added later)

This standard was originally published in 1959 and subsequently revised in 1984. The 1959 version was published as methods of test for ash of coal and coke, when the country did not possess much systematic data of analysis of coal and coke and thus the standard provided basis for further investigational work.

With the latest development in the field, the committee responsible for the preparation of this standard decided to revise it. The first revision was taken up to modify the title of the standard as 'Methods of determination of the chemical composition of ash of coal and coke' so as to emphasize that it deals with the methods of determination of only chemical composition of ash of coal and coke and therefore the clause dealing with fusibility of ash was deleted. The Committee also concluded that preparation of a separate standard may be taken up subsequently when more data is available on the basis of sophisticated equipment such as Leitz Heating Microscope or atomic absorption, spectrophotometer, etc. Considerable assistance was derived from ISO 1171:1981 'Solid mineral fuels determination of ash', during the first revision.

In this (second) revision, the following modifications have been taken up:

- Incinerated temperature referred in ash terminology has been modified to 815 ± 10 °C, instead of 810 ± 15 °C.
- For method of sampling for coal has been referred by IS 16143 (Part 2); IS 16143 (Part 3) and IS 16143 (Part 4) and for coke has been referred by IS 16143 (Part 5) and IS 16143 (Part 6) as the erstwhile referred standard IS 436 (Part 1/ Sec 2) and IS 436 (Part 2) has been withdrawn.
- editorial changes have been made.

The Committee has separately formulated IS 5062 (Part 2) to prescribe methods of determination of ash in brown coals and lignites.

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 : 2022 ‘Rules for rounding off numerical values (*second revision*)’.

1 SCOPE

1.1 This standard prescribes the methods of test for the analysis of ash of coal and coke. The standard contains definitions of terms and methods of preparation of ash.

1.2 Should any inconsistency exist between the requirements of this standard and those, if any, given in standards for individual materials, the latter shall prevail.

1.3 Test methods not described in this standard, and not specified in the standard for individual materials shall be subject to agreement between the purchaser and the vendor.

2 REFERENCES

The following standards contain provisions which through reference in this text, constitute the provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standard indicated below:

<i>IS No.</i>	<i>Title</i>
IS 264 : 2005	Nitric acid — Specification (<i>third revision</i>)
IS 265 : 2021	Hydrochloric acid — Specification (<i>fifth revision</i>)
IS 266 : 1993	Sulphuric acid — Specification (<i>third revision</i>)
IS 321 : 1964	Specification for absolute alcohol (<i>first revision</i>)
IS 323 : 2009	Rectified spirit for industrial use — Specification (<i>second revision</i>)
IS 4311 : 2024	Coal — Determination of mineral matter (<i>first revision</i>)
IS 1070 : 2023	Reagent grade water — Specification (<i>fourth revision</i>)
IS 16143 (Part 2) : 2021/ISO 13909-2 : 2016	Hard coal and coke — Mechanical sampling: Part 2 Coal — Sampling from moving streams (<i>first revision</i>)

IS 16143 (Part 3) : 2021/ISO 13909-3 : 2016	Hard coal and coke — Mechanical sampling: Part 3 Coal — Sampling from stationary lots (<i>first revision</i>)
IS 16143 (Part 4) : 2021/ ISO 13909-4 : 2016	Hard coal and coke - Mechanical sampling: Part 4 Coal — Preparation of test samples (<i>first revision</i>)
IS 16143 (Part 5)) : 2021/ISO 13909-5 : 2016	Hard coal and coke — Mechanical sampling: Part 5 Coke — Sampling from moving streams (<i>first revision</i>)
IS 16143 (Part 6) : 2021/ISO 13909-6 : 2016	Hard coal and coke - Mechanical sampling: Part 6 Coke — Preparation of test samples (<i>first revision</i>)
PCD/07/19732	Methods for sampling of coal and coke: Part 1 Sampling of coal: Section 1 Manual sampling [<i>second revision of IS 436 (Part 1/Sec 1)</i>]
PCD/07/24223	Methods of test for coal and coke: Part 1 Proximate analysis (<i>third revision IS 1350 (Part 1)</i>]

3 TERMINOLOGY

3.1 For the purpose of this standard the following definitions shall apply.

3.1.1 *Ash* — Inorganic residue left when powdered coal or coke is incinerated in air to constant mass at $(815 \pm 10) ^\circ\text{C}$.

3.1.2 Ash as determined is not the same as the original mineral matter associated with the coal, because changes take place during incineration, namely, the loss of combined water, or carbon dioxide from carbonates, etc. Recommended formulae for the calculation of mineral matter in coal from ash are given under **8** of IS 4311.

4 QUALITY OF REAGENT

4.1 Unless specified otherwise, pure chemicals (*see* Note) shall be employed and distilled water, conforming to IS 1070 shall be used where the use of water as a reagent is specified.

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

5 SAMPLING

5.1 Methods of Sampling

Methods of sampling shall be as prescribed in PCD/07/19732 for manual sampling of coal, IS 16143 (Part 2) for coal sampling from moving streams, IS 16143 (Part 3) for coal sampling from stationary lots, IS 16143 (Part 4) for preparation of coal test samples and IS 16143 (Part 5) and IS 16143 (Part 6) for coke sampling and preparation of test sample respectively.

5.2 Preparation of Samples for Test

5.2.1 General

Methods of sampling prescribed in **5.1** shall have been followed in the preparation of samples of coal and coke sent to the laboratory.

5.2.2 The analysis sample prepared in accordance with **5.1** shall consist of 0.5 kg of air-dried coal or coke ground to pass IS sieve 20.

5.2.3 The percentage loss of moisture in air-drying shall be required to be recorded on the label together with the method of sampling used.

5.2.4 Samples which are received in the laboratory already ground to pass IS sieve 20 (212 microns) shall be re-sieved to verify that all the material passes this sieve, and then air-dried for 24 h and mixed and bottled. When a sample of coal or coke be transported to any distance between the point of preparation and the laboratory under conditions in which it may be shaken down and may cause segregation to any degree, the entire contents of the bottle shall be re-mixed before analytical work is started. The use of mechanical devices is recommended.

5.2.5 The normal method of mixing coal or coke in the laboratory is to roll it on a sheet of rubber cloth, and to turn it over at intervals with a large spatula or flat spoon. This method is not entirely satisfactory, since the movement of the coal tends to cause segregation. The difficulty may be overcome in part by spreading the mixed sample in a thin layer and filling the analysis bottle by means of small increments taken with the spoon from spaces spaced uniformly over the surface of the layer. This method of filling is particularly necessary when more than one bottle is being filled. A laboratory mechanical mixer is, however, preferable.

5.2.6 In case an analysis sample ground to pass IS sieve 20 (211 microns) is not received in the laboratory, a sample of air-dried material shall be prepared from the sample of coal or coke received in the laboratory in the manner prescribed under **A-3** of IS 1350 (Part 1) and the loss of moisture on air-drying recorded.

6 GENERAL

6.1 Ash

As prepared in the laboratory by the incineration of powdered coal or coke in an oxidizing atmosphere. It consists mainly of oxides of silicon, aluminum, iron, calcium, magnesium and sulphur, with smaller amounts of alkalis, and the oxides of titanium, manganese, phosphorus and arsenic. Some of the oxides are present in the free-state and others are combined to form silicates, sulphates, phosphates and arsenates. The recognized analytical methods for the quantitative analysis of mixtures of inorganic oxides are also applicable to the constituents of coal ash and coke ash. The scheme of analysis for coal and coke ashes is, however, considerably simpler than schemes for the analysis of silicate minerals in general. For example, the first two analytical groups are not included and only one separation of group members is necessary, namely, for sodium and potassium.

6.2 Ash prepared from a coke usually represents, in ultimate composition the ash from the corresponding coal, the main point of difference being the presence of more of sulphate in coke ash.

6.3 The main analysis which consists of the determination of silicon, barium, iron, aluminum, titanium, calcium and magnesium can be carried out on one portion of ash as described under **7.1** to **7.13**. Determination of manganese, phosphorus, alkalis and sulphur, when required, are carried out on separate portions of ash as described under **7.14** to **7.17**.

6.4 Preparation of Ash for Analysis (*see also 7.3 and 7.4*)

6.4.1 Ash prepared in different ways from the same coal may differ appreciably in composition. For example, coal incinerated at a dull-red heat may give an ash containing carbonates which would be decomposed quantitatively at higher temperatures. Again, when thick layers of powdered coal are incinerated, reducing conditions bring about the formation of sulphides which are oxidized only with difficulty; also, a greater amount of sulphur may be retained in the ash than is the case when the coal is incinerated in thin layers.

6.4.2 The conditions specified for the determination of the ash content of coal or coke [*see 9.3* of IS 1350 (Part 1)] ensure the reproducibility of results in different laboratories. Thin layers of coal or coke are incinerated at $(815 \pm 10)^\circ\text{C}$ in an oxidizing atmosphere until the residue is constant in mass. Under these conditions of preparation, the ash should be free from carbonates and from all but small traces of sulphide, but all the iron compounds should be fully oxidized. When the method is used, however, for the preparation of an appreciable quantity of ash for analysis it is tedious, extremely so with low-ash fuels.

6.4.3 This tedium may be avoided by the preparation of two separate samples of ash for analysis, if certain precautions are observed. The separate samples are referred to as standard ash and bulk ash:

- a) Prepare the standard ash in the standard manner [*see 9.3* of IS 1350 (Part 1)] and determine the moisture and ash contents of the fuel during the preparation. Use the standard ash for the determination of sulphur in the ash.
- b) Prepare the bulk ash by any non-standard method. Ascertain the moisture contents of the fuel and determine the ash content, as prepared by the non-standard method.
- c) Correct all analytical results obtained on the bulk ash to the standard ash basis: the presence of carbonates or sulphides, if any, in the ash prepared by the non-standard method being ignored. The results shall be multiplied by the fraction given below:

$$\frac{\text{Percentage of bulk ash on the dry – fuel basis}}{\text{Percentage of standard ash on the dry – fuel basis}}$$

6.5 General Precautions and Instructions

6.5.1 Good-quality apparatus, particularly glassware, is an essential requirement for the accurate analysis of ash. If porcelain dishes are used where platinum is not available, they should be kept specially for this purpose and care should be taken to ensure that the glaze is undamaged. All reduction in particle size of the ash should be carried out in an agate mortar.

6.5.2 Desiccators should be recharged frequently with the desiccating agent. Ignited residues, which often act as dehydrating agents, should not be allowed to remain in desiccators before weighing for longer periods than are necessary for cooling. Usually, a period of 15 min to 30 min is sufficient.

6.5.3 Special attention is called to the care necessary in any operations involving the use of perchloric acid. This acid, particularly when over 70 percent in strength, or when hot, combines with organic matter or easily-oxidizable inorganic matter, sufficiently violently lead to serious explosions. Explosions may also be caused by the vapours of the heated acid. Great care, therefore, should be taken to avoid the contact of this acid with grease, dust, or rubber stoppers, etc., and to ensure that all apparatus used in operations involving perchloric acid is scrupulously clean. This applies particularly to the lip of acid storage bottle.

6.5.4 All reagents used should be of the highest purity obtainable; in this respect, particular attention should be given to the ammonium hydroxide. Reference to 'water' means distilled water, which should be free from dissolved gases.

6.5.5 When ash analysis is being undertaken for the first time, duplicate blank determinations should be carried out with all methods, using the same reagents and laboratory conditions as in the actual analysis; the results obtained should be applied as corrections to the ash analysis. When new stocks of reagents are obtained or laboratory conditions change, new blank determinations should be carried out. Until operators are well trained in the technique of ash analysis, it is advisable to carry out duplicate analysis on each sample.

6.6 Methods — Two schemes of analysis and procedures are described. Of these, the scheme and procedures described under **8** are quicker and may be adopted where applicable. In case of dispute, the scheme and procedure prescribed under **7** shall be adopted for referee purposes.

7 REFEREE METHODS

7.1 Apparatus

7.1.1 *Shallow Silica Dishes*, 5 cm in diameter and 1 cm deep

7.1.2 *Silica Basins*, 15 cm × 9 cm

7.1.3 *Platinum Crucible*, about 30 ml in capacity

7.1.4 *Hot Air Bath*, illustrated in Fig. 1

It is constructed of sheet iron the base being welded to the sides. Nichrome wire is suitable to support the crucible provided it has been heated initially to dull-red heat to prevent possible staining of the crucible. In use, the bath is supported by resting the loose metal flange on a tripod stand and the base is heated to just below dull-redness.

7.1.5 Platinum Basin — about 150 ml in capacity

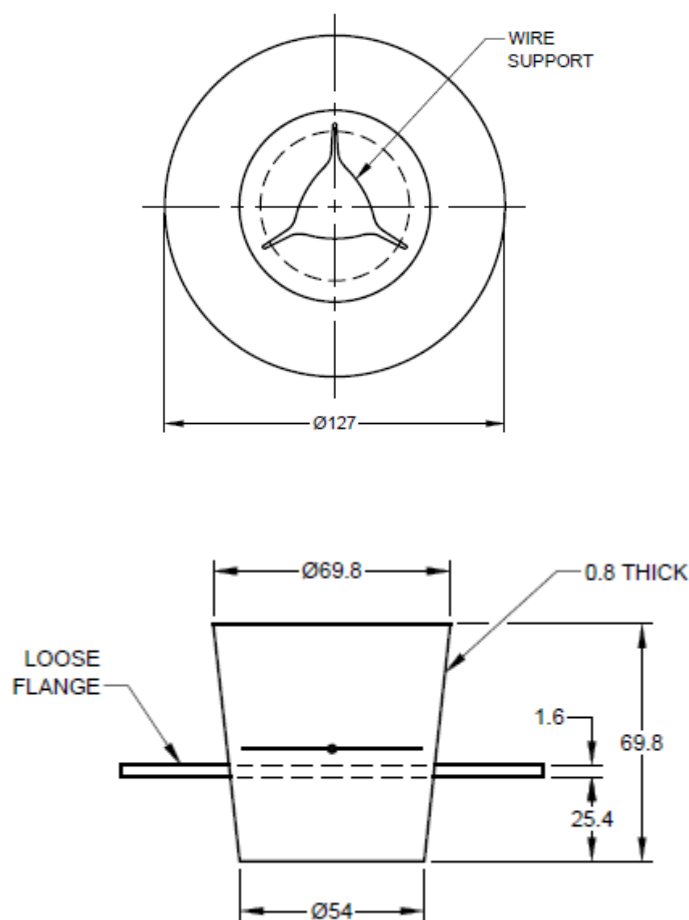


FIG. 1 HOT AIR BATH FOR USE WITH CRUCIBLES

7.1.6 Filter Papers

- a) Rapid, low ash, such as Whatman No. 40, 41;
- b) Fine, low ash, such as Whatman No. 42; and
- c) Toughened, such as Whatman No. 541.

7.1.7 Reductor for Titanium Determination — The apparatus shown in Fig. 2, consists of a short-stemmed, 200 ml, separating funnel, fitted with a rubber bung carrying a short length of glass tube corked at the upper end. The stem is attached by means of a rubber tubing to a glass bulb of about

25 ml capacity, leaving about 5 cm of the tubing fitted with a spring clip, between the glass parts. The ends of the separating funnel and the glass bulb should be riffled and the rubber tubing wired on.

7.2 Reagents

7.2.1 Concentrated Hydrochloric Acid, specific gravity 1.16 (conforming to IS 265)

7.2.2 Dilute Hydrochloric Acid, one volume of concentrated hydrochloric acid diluted with nine volumes of water.

7.2.3 Sodium Carbonate, anhydrous

7.2.4 Hydrogen Peroxide

It is pure and, therefore, unstabilized, of 100 volume strength. It is essential that this reagent should be supplied and stored in waxed bottles.

7.2.5 Ammonium Sulphate Solution, in water, containing 100 g of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ per litre.

7.2.6 Concentrated Sulphuric Acid, conforming to IS 266 and containing about 98 percent by mass of sulphuric acid (H_2SO_4).

7.2.7 Sulphuric Acid (1:1), one volume of concentrated sulphuric acid diluted by pouring very carefully in one volume of water.

7.2.8 Dilute Sulphuric Acid, one volume of concentrated sulphuric acid diluted with four volumes of water.

7.2.9 Weak Sulphuric Acid, containing 55 ml of concentrated sulphuric acid per litre.

7.2.10 Hydrofluoric Acid, a solution in water, containing about 550 g of hydrofluoric acid per litre, free from phosphorus.

7.2.11 Ammonium Sulphate, solid

7.2.12 Concentrated Ammonium Hydroxide Solution, specific gravity 0.90

7.2.12.1 Bench bottles of ammonium hydroxide often contain appreciable quantities of impurities, usually silica and ammonium carbonate, the former being a result of attack on the glass and the latter arising from unnecessary exposure to air. Contamination by these two impurities can be avoided by purchasing pure reagent, storing it in waxed bottles, and taking care to replace stoppers promptly after use.

7.2.13 Dilute Ammonium Hydroxide Solution, one volume of concentrated ammonium hydroxide solution diluted with nine volumes of water.

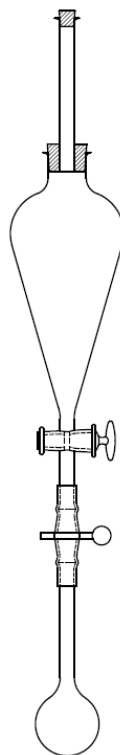


FIG. 2 REDUCTOR FOR TITANIUM DETERMINATION

7.2.14 Weak Ammonium Hydroxide Solution, one volume of dilute ammonium hydroxide solution diluted with nine volumes of water.

7.2.15 Indicator Thread, white thread impregnated with an alcoholic solution of methyl red so that the thread, when dried, assumes a strong pinkish-red colour with acid vapours. Use in about 5 cm lengths.

7.2.16 Ammonium Nitrate Solution, containing 2 g of ammonium nitrate (NH_4NO_3) per litre and made alkaline to methyl red by adding one drop of concentrated ammonium hydroxide solution in excess.

7.2.17 Methyl Red Indicator, 1 g of methyl red dissolved in 200 ml of rectified spirit, 95 percent by volume (conforming to IS 323).

7.2.18 Sodium Pyrosulphate, solid

Alternatively, potassium pyrosulphate may be used.

7.2.19 Potassium Permanganate Solution, approximately 0.1 N, to be standardized against standard sodium oxalate solution.

7.2.20 Ammonium Thiocyanate Solution, containing 400 g of ammonium thiocyanate (NH_4CNS) in 500 g of water.

7.2.21 Mercurous Nitrate Solution

It is approximately 0.1 N obtained by dissolving 30 g of mercurous nitrate ($\text{HgNO}_3 \cdot \text{H}_2\text{O}$) in 1 liter of 5 percent (v/v) solution of nitric acid and standardized as described below. The nitric acid should be free from oxides of nitrogen which can be eliminated by boiling with a few crystals of urea.

7.2.21.1 Standardization

Take 25 ml of a decinormal solution of ferrous ammonium sulphate, add 20 ml of dilute sulphuric acid and cool to about 10 °C. Add potassium permanganate solution until the iron is oxidized and there is so small an excess of permanganate that the pink colour fades away quickly. Add 15 ml of ammonium thiocyanate solution and allow the liquid to attain room temperature. Titrate with a solution of mercurous nitrate, shaking vigorously throughout the titration, until the colour of ferric thiocyanate is just discharged.

7.2.22 Ferrous Ammonium Sulphate Solution

It is approximately 0.1 N (containing 39 g of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ per litre of weak sulphuric acid), standardized against potassium permanganate solution (*see 7.2.19*).

7.2.23 Zinc Amalgam

To prepare the amalgam, wash 15 g of small granulated zinc with weak sulphuric acid and heat the washed zinc pieces with 300 g of mercury for 1 h on a water-bath. Stock may be preserved under weak sulphuric acid. Use only the liquid form of the amalgam, separated from the solid form by passing through a tap with a fine bore. Allow to stand for several hours before using amalgam which has been used in a reduction, may be recovered by adding it to the solid amalgam from which the liquid amalgam has been separated.

7.2.24 Sodium Bicarbonate Tablets

Each about 0.8 g in mass. The tablets may be prepared from slightly-damped sodium bicarbonate in a press such as is used in the briquetting of coal prior to the determination of calorific value.

7.2.25 Ferric Sulphate Solution, approximately 0.02 N, standardized against pure titanium dioxide (TiO_2) as in **7.9**.

7.2.26 Potassium Thiocyanate Solution, saturated, containing about 217 g of potassium thiocyanate (KCNS) in 100 ml of water.

7.2.27 *Hydrogen Sulphide*, gas from a kipp

7.2.28 *Ammonium Chloride Solution*, in water containing only a trace of ammonium chloride.

7.2.29 *Bromine Water*, saturated

7.2.30 *Saturated Ammonium Oxalate Solution*, in water, containing about 42 g of ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ per litre.

7.2.31 *Dilute Ammonium Oxalate Solution*, one volume of saturated solution diluted to 100 volumes.

7.2.32 *Di-sodium Hydrogen Phosphate (Sodium Phosphate) Solution*, in water containing 100 g of disodium hydrogen phosphate $(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O})$ per litre.

7.2.33 *Concentrated Nitric Acid*, specific gravity of 1.42 (see IS 264)

7.2.34 *Dilute Nitric Acid*, one volume of concentrated nitric acid diluted with three volumes of water.

7.2.35 *Weak Nitric Acid*, three volumes of concentrated nitric acid diluted with 100 volumes of water, boiled for 10 min and cooled.

7.2.36 *Standard Nitric Acid*, approximately 0.1 N obtained by diluting 64 ml of concentrated nitric acid with water to 1 litre and standardizing against pure, anhydrous, sodium carbonate using methyl orange as an indicator.

7.2.37 *Sodium Bismuthate*, containing at least 4 percent of active oxygen which corresponds to 70 percent of sodium bismuthate (NaBiO_3) .

7.2.38 *Ammonium Molybdate Solution*

Dissolve 100 g of pure molybdic acid (containing not less than 85 percent of MoO_2) in a mixture of 400 ml cold water and 80 ml of concentrated ammonium hydroxide solution. Mix the solution by shaking and pour slowly into a solution of 400 ml of concentrated nitric acid in 600 ml of water, contained in a flask. Mix by shaking during the addition. Add to the mixture about 0.05 g of microcosmic salt $[\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}]$ dissolved in a small quantity of water. Heat the mixture gently to 65 °C, shaking frequently. Allow the solution to cool, and leave it to stand overnight, then decant the clear supernatant liquid into a dark-brown stoppered bottle. Do not keep the reagent longer than two months.

7.2.39 *Potassium Nitrate Solution*, neutral, containing 1 gm of potassium nitrate $[\text{KNO}_3]$ per litre.

7.2.40 *Standard Sodium Hydroxide Solution*, approximately 0.1 N, in water, standardized against decinormal nitric acid stored in an atmosphere free from carbon dioxide.

7.2.41 *Phenolphthalein Indicator, Neutral*, containing 0.5 g of phenolphthalein dissolved in 100 ml of 95 percent rectified spirit (*see* IS 323) and add a dilute solution of sodium hydroxide drop by drop until the colour turns faint pink.

7.2.42 *Ammonium Chloride*, solid, free from alkalis as far as possible.

7.2.43 *Calcium Carbonate*, precipitated, free from alkalis as far as possible.

7.2.44 *Concentrated Barium Chloride Solution*, containing 100 g of barium chloride [BaCl₂·2H₂O] per litre.

7.2.45 *Dilute Barium Chloride Solution*, one volume of concentrated barium chloride solution diluted to ten volumes with water.

7.2.46 *Ammonium Carbonate Solution*, in water containing 100 g of ammonium carbonate [(NH₄)₂CO₃] per litre.

7.2.47 *Perchloric Acid*, a solution in water containing about 60 g of perchloric acid (HClO₄) per 100 g of solution.

CAUTION — Great care shall be taken when using this reagent (*see* 6.5.3).

7.2.48 (a) *Ethyl Acetate*, free from ethyl alcohol, with a purity of 99.7 percent to 100 percent.

or

(b) *Absolute Alcohol*, saturated with potassium perchlorate.

7.3 Determination of Ash Content and Preparation of Standard Ash for Determination of Sulphur

Accurately weigh into the shallow silica dish, 1.00 g to 1.01 g of coal or coke of known moisture content and ground to pass IS sieve 20 (211 microns). Place it in a muffle furnace at room temperature and raise the temperature to (500 ± 15) °C in 30 min. Maintain at this temperature for 30 min and then heat in an oxidizing atmosphere at (815 ± 10) °C for 1 h, or until constant in mass. After incineration cover the dish and transfer the covered dish to a desiccator and allow to cool by the side of the balance. When cool, weigh the dish, brush out the ash into a beaker ready for the determination of sulphur (*see* 7.17) and reweigh the empty dish. Obtain the mass of ash by difference and note the result as a percentage of coal and coke. Repeat the determination until a sufficient quantity (1.0 g) of ash has been prepared.

7.4 Preparation of Bulk Ash for General Ash Analysis

7.4.1 Weigh, to the nearest 0.01 g, sufficient coal or coke, of known moisture content, to yield enough ash for the main analysis. Transfer to silica basins. Arrange the sample in small heaps and ignite it in the open with a flame or in a muffle furnace. Allow the heaps to smoulder for a few hours to destroy any coking power that the coal may possess. For coals which do not readily

smoulder, heat in a muffle furnace from cold to the required temperature at a rate that avoids decrepitation. Break up the heaps, if necessary, and complete the incineration in a muffle furnace previously heated to the required temperature. After incineration, allow the ash to cool in a place free from draughts. When cold, transfer to a tared weighing bottle and weigh, removing the last particles with a brush. Grind the ash as fine as possible, mix thoroughly and transfer the ash to an air-tight specimen tube. Calculate the percentage of bulk ash in the dry coal.

7.4.2 For coals, a temperature of 550 °C to 600 °C provides ash which is relatively easily dissolved. For high-temperature cokes a temperature of 775 °C, with occasional stirring of the mass to give all the ash access to air, is necessary to avoid too protracted an incineration. From 3 g to 8 g of ash will be required for the main analysis. The moisture content must be determined on a separate portion. The whole of the ash for general analysis may be prepared by the standard method if preferred. No correlation factor [see **6.4.3** (c)] is required in this case but care shall be taken to ensure that moisture and carbon dioxide picked up during grinding are removed by incineration for 30 min at (815 ± 10) °C before weighing out ash for analysis.

7.5 Solution of Ash and Determination of Silica and Barium Oxide

7.5.1 Accurately weigh 1.0 g to 1.1 g of ash (see **7.4**) in a platinum crucible or a hard glass beaker. Cover the ash with 10 ml of concentrated hydrochloric acid, allow to digest at the boiling point covering the crucible with its lid and continue the digestion on the hot-air bath until about half the liquid has been evaporated. Further, add 5 ml of the acid and again digest at the boiling point to half bulk. Add another 5 ml of concentrated hydrochloric acid and continue the digestion until only 2 ml or 3 ml of liquid remain.

7.5.2 Transfer the crucible and the lid to a platinum basin, containing 75 ml to 100 ml of hot water. Turn the crucible on its side and digest at the boiling point or just below for about 20 min, protecting the liquid from contamination by dust in this and subsequent operations. Remove the crucible and lid, wash them clean with hot water, and filter the hot liquid through a fine, low-ash, filter paper in to a platinum basin. Wash the residue five times with hot water, collecting the washings with the filtrate. Evaporate on a water bath.

NOTE — Platinum vessels should be used to preclude contamination by silica from glassware. If glassware is used it should be of good quality resistance glass and inside surfaces should be free from scratches or chips. Blank determinations of the silica extracted from the glass under the conditions of the method must be made. Cover glasses are usually made of soft glass and yield a little soluble silica.

7.5.3 Transfer the wet filter paper and the residue to a platinum crucible and after gentle heating, incinerate at a dull-red heat. Allow to cool and mix the residue thoroughly in the crucible with 4 g of anhydrous sodium carbonate. Cover the crucible with its lid and heat by means of an ordinary burner until fusion point is reached. Raise the temperature of the fused mass to about 1 000 °C at a rate which avoids excessive turbulence, maintain at this temperature until the liquid is quiescent after which heat for about 30 min at a temperature not below 1 100 °C. Avoid admitting reducing gases into the crucible, by tilting it during the early stages of heating. If a blow-pipe is used in the final stage, direct the flame at an angle against the side and bottom so that it does not envelop the crucible. Should the reduction of iron compounds lead to the formation of a platinum-iron alloy

which is seen as a black stain on ignition, remove by alternate ignition and extraction with concentrated hydrochloric acid.

7.5.4 Allow the crucible to cool, then heat rapidly to about 400 °C and immediately plunge the lower two-thirds of the crucible into cold water to loosen the melt. If necessary, repeat. Immerse the crucible in sufficient hot water to cover it, contained in a platinum basin. Add the crucible lid. Cover the basin and slowly add 15 ml of concentrated hydrochloric acid. Break up any mass or silica with a glass rod. Add one or two drops of hydrogen peroxide to decompose any manganic acid which may have come from manganates formed during the fusion. Heat the liquid gently to boiling point and remove the cover glass, washing the underside into the liquid. Lift out the crucible and lid by means of a thin glass rod, washing each into the liquid. Clean the inside of the crucible with water and a rubber tipped glass rod, adding the washings to the liquid. Add 10 ml of ammonium sulphate solution.

7.5.5 Transfer the liquid and precipitate to the vessel in which the acid solution of the ash has been evaporating (*see 7.5.2*). Evaporate the whole to dryness on a water-bath. To hasten the process, break-up occasionally the crust formed on the solution and when nearly dry, break-up the crystal by pressing with a flat-ended glass rod. This minimizes the time of drying. Cool, cover the basin and add 10 ml of concentrated hydrochloric acid, followed, after 2 min to 3 min, by 90 ml of hot water. Remove the cover glass, washing the underside into the liquid. Heat the liquid to boiling point and maintain it at the boiling point for 10 min. Decant the supernatant liquid through a rapid, low-ash, filter paper. Subsequently washing the residue on to the paper. Retain the filtrate. Wash the residue with hot, dilute hydrochloric acid until the paper is white and then three times with hot water. Retain the residue. Replace the washings and filtrate into the basin used for evaporation and evaporate to dryness on a water-bath. Transfer the covered basin to an oven maintained at 110 °C and heat for 1 h.

7.5.6 Cool, cover the basin and add 5 ml of concentrated hydrochloric acid and digest on a water-bath for 10 min. Add 90 ml of hot water and remove the cover. Allow to boil gently until the precipitate is white, breaking up any lump with a flat-ended glass rod. Filter the liquid through a rapid, low-ash, filter paper, subsequently washing the residue on to the paper. Wash the residue with hot, dilute, hydrochloric acid until the paper is white and then three times with hot water. Retain the filtrate and washings.

7.5.7 Place the washed precipitates along with papers obtained in **7.5.5** and **7.5.6** into a platinum crucible without preliminary drying. Heat the crucible gently so that the papers char without flaming. When the carbon has been burnt away, cover the crucible with its lid in such a way that air is not excluded and raise the temperature to about 1 200 °C. Heat at this temperature for 20 min and cool in a desiccator. Weigh immediately when cool and repeat the ignition to constant mass.

7.5.8 Moisten the ignited residue with water and cautiously add three drops of concentrated sulphuric acid followed by 10 drops of hydrofluoric acid. Place the lid on the crucible and heat gently on the hot-air bath to drive off the acid. Raise the temperature of the residue to 800 °C and allow to cool. Add one drop of concentrated sulphuric acid followed by five drops hydrofluoric acid and ignite as before. Cool in a desiccator and weigh. Repeat the second acid treatment and ignite to constant mass. The total loss in mass caused by the acid treatment represents the amount

of silica, except for traces which may have escaped separation and which are recovered subsequently (*see 7.7.2*).

7.5.9 Dissolve the residue or stain in the crucible by fusion with sufficient amount of sodium carbonate, to allow rinsing of the crucible walls with the melt. Continue the fusion for 10 min. Cool and dissolve the melt in 100 ml of boiling water containing a slight excess of hydrochloric acid. Clean the crucible with a rubber-tipped glass rod. Add 5 ml of ammonium sulphate solution. If a white precipitate is obtained continue boiling for 5 min and allow to stand for 4 h in a platinum basin. Remove precipitate by filtering through a fine, low-ash, filter paper or through asbestos in a gooch crucible and determine it as barium sulphate in the normal way. Express the barium as barium oxide.

7.5.10 Add the filtrate from the barium separation, or the solution of the melt, if this is clear, to the filtrate from the silica separation (*see 7.5.6*).

7.6 Recovery of Traces of Silica and Determination of Oxides of Iron Group

7.6.1 To the combined filtrates and washings (*see 7.5.6* and **7.5.10**) add 2 g to 3 g of ammonium chloride, heat to incipient boiling and continuously add concentrated ammonium hydroxide solution drop by drop, stirring briskly with a rubber tipped glass rod, until the red colour of colloidal ferric hydroxide is seen. Test the liquid with an indicator thread and continue to add ammonium hydroxide drop-wise with brisk stirring until the liquid is just alkaline. If an excess of ammonium hydroxide is added accidentally, or if the liquid is found to be alkaline on first testing, add concentrated hydrochloric acid drop by drop until one drop changes the indicator colour to pinkish-red. Then proceed with the addition of ammonium hydroxide drop-wise.

7.6.2 Raise the temperature of the liquid to just boiling, remove immediately from the source of heat or keep the covered solution at a lower temperature for 5 min to 10 min and then allow to stand at room temperature till the precipitate has settled. Boiling makes the precipitate slimy which settles very slowly. Decant the supernatant liquid through a rapid, low-ash filter paper and transfer the precipitate to the paper. Removal of the last traces of precipitate is not necessary. Wash twice with a cold solution of ammonium nitrate and then twice with hot water. After the last washing has drained, remove the beaker containing the filtrate and replace the beaker used in the precipitation (*see 7.6.1*). Evaporate the filtrate to 50 ml to 100 ml on a hot plate.

7.6.3 Push a hole through the bottom of the filter paper with a thin glass rod and place the rod in the beaker below. Wash as much as possible of the precipitate to the beaker using the minimum quantity of water directed in a strong fine jet. Rinse the filter paper with 3 ml portions of concentrated hydrochloric acid, washing with hot water and each rinsing, until the paper is white. Digest the acid mixture at incipient boiling until the precipitate has dissolved, meanwhile incinerate the filter paper in a platinum crucible and add the ash to the acid solution. Dilute the acid mixture to about 300 ml with freshly heated water and repeat the precipitation with concentrated ammonium hydroxide solution exactly as described under **7.6.1** and **7.6.2**. Allow to stand only as long as is necessary for settling.

7.6.4 Decant the supernatant liquid through a rapid, low-ash, filter paper and transfer the precipitate to the paper. Complete the transfer of the precipitate from the beaker by cleaning the inside with about 3 ml of hot water to which one drop of concentrated hydrochloric acid has been added, using a rubber-tipped glass rod. Wash down the sides of the beaker and the glass rod, add one drop of methyl red indicator and make just alkaline with dilute ammonium hydroxide solution. Transfer the whole on to the filter paper. Wash the total precipitate five times with ammonium nitrate solution and finally three times with cold water. Dry the precipitate and paper in an oven at 100 °C to 105 °C.

7.6.5 Add the filtrate and washings to the filtrate obtained under **7.6.2** and evaporate to half the original bulk. If further precipitation of hydroxides occurs on concentration, make it acidic with concentrated hydrochloric acid and add a slight excess of concentrated ammonium hydroxide solution. Filter off any precipitate and wash as described under **7.6.4**. If the precipitate is pinkish or brownish-red a double precipitation is necessary. Dry the precipitate and paper in an oven at 100 °C to 105 °C. Retain the filtrate for separation of platinum and manganese (*see 7.11*).

7.6.6 Separate the dry precipitate under **7.6.4** from its paper and transfer the latter together with the dried paper containing any precipitate under **7.6.5** to a weighed platinum crucible. Char the paper without flaming, finally removing the residual carbon at a bright-red heat. Cool, add the separated precipitate and heat at 1 100 °C to constant mass. Deduct the mass of the filter-paper ash, the remainder is the mass of oxides of iron, aluminum, titanium, silicon and phosphorus.

7.7 Analysis of the Iron Group-Solution of the Group and Determination of Traces of Silica

7.7.1 To the crucible containing the oxides add about 5 g to 7 g of powdered sodium or potassium pyrosulphate and cover the crucible with its lid. Heat sufficiently to keep the pyrosulphate just melted. After 15 min raise the temperature slowly, to avoid excessive frothing, to below dull-red heat and maintain at this temperature until the melt appears to be clear. Cool and transfer to a suitable glass beaker. Cover the crucible with water and cautiously add 20 ml of concentrated sulphuric acid. Digest at the boiling point for two or three minutes, then dilute to 150 ml with water and continue the digestion on a water-bath until the melt has dissolved. Remove the crucible and lid, washing each into the liquid. If there is an insoluble residue, filter the solution through a toughened filter paper. Wash the residue five times with water and ignite it in a platinum crucible. Fuse the residue with 2 g of pyrosulphate as described above. Dissolve this melt in the solution of the first pyrosulphate melt and, having removed the crucible and lid, evaporate the solution until fumes of sulphuric acid are evolved, then allow to cool.

7.7.2 Cautiously dilute the 'fumed' liquid to about 200 ml with water; heat and filter through a rapid, low-ash, filter paper. Wash the precipitate seven times with hot water. Evaporate the filtrate, protected with a cover glass to about 150 ml. Ignite the precipitate and paper at about 1 200 °C in a platinum crucible to constant mass. Treat the residue with one drop of concentrated sulphuric acid and 4 drops of hydrofluoric acid and volatilize the silica, if any, in the manner described under **7.5.8**. The mass of silica volatilized must be added to the previous mass of silica to obtain the total silica present in the ash.

7.7.3 Add about 1 ml of concentrated sulphuric acid to the residue and heat to 'fuming' for a few seconds. Cool and cautiously dilute to about 15 ml, filter through a rapid filter paper into the solution of pyrosulphate melt obtained under **7.7.2** washing any residue twice with water. Discard the residue. Transfer the solution of pyrosulphate melt to a 250 ml calibrated flask, make up the volume with water and mix thoroughly.

7.8 Determination of Iron Oxide

Transfer 100 ml, accurately measured, of the 250 ml solution of the iron group to a glass-stoppered conical flask. Cool the solution to below 10 °C and add a few drops of potassium permanganate solution to ensure that the iron is oxidized completely, taking care to add only one drop in excess so that the pink colour will fade quickly. Warm to room temperature, add, 15 ml of a solution of ammonium thiocyanate and shake it thoroughly. Titrate with the standardized solution of mercurous nitrate, shaking well throughout the titration, until the colour of ferric thiocyanate is just discharged. Calculate on the basis that 1 ml of decinormal mercurous nitrate solution is equivalent to 0.007 984 g of ferric oxide (Fe_2O_3).

7.9 Determination of Titanium Dioxide

Detach the glass bulb from the reductor (*see 7.1.7*) and fill it with air-free water. Re-attach it to the apparatus and with the spring clip and funnel tap both open, fill the tubing up to the tap with air-free water poured through the funnel. The air may be displaced from the tubing by pinching. Close the clip and then tap, and pour out the excess water in the funnel. Introduce into the funnel 100 ml of the solution of the iron group (*see 7.7.3*), 40 ml of weak sulphuric acid and 20 ml of zinc amalgam. Add one tablet of sodium bicarbonate and immediately fix the uncorked tube in the top of the funnel. As soon as effervescence has ceased, add the broken portions of another bicarbonate tablet down the glass tube. When effervescence is just ceasing, fit the cork to the top of the glass tube. Shake the apparatus vigorously for 10 min to 15 min. This is the most important part for the determination. It is essential that the apparatus should be shaken sufficiently vigorously to throw the amalgam up into the aqueous layer-swirling motion is useless. Ease the top cork a little, every 2 min, to release excess pressure. Replace the apparatus in a stand. Fill a burette with 0.02 N solution of ferric sulphate. Open the spring clip (the apparatus remains closed to the air) and then the tap of the funnel. By alternately pinching and releasing the rubber tubing, make the amalgam drop into the bulb, air-free water being displaced. Close the funnel tap as the last of the amalgam passes through and detach the bulb and the spring clip. Uncork the top glass tube and pour 5 ml of potassium thiocyanate solution down the tube. Remove the tube and the bung, and rapidly titrate the solution *in situ* with the solution of ferric sulphate until the pinkish colour persists for 1 min. Calculate on the basis that 1 ml of 0.02 N solution of ferric sulphate is equivalent to 0.001 598 g of titania (TiO_2).

7.10 Estimation of Alumina

The amount of phosphate in the ash is determined on a separate portion of ash as described under **7.15**. If the amount, together with the amount of silica (*see 7.7.2*), ferric oxide (*see 7.8*), titania (*see 7.9*), is deduced from the total mass of oxides (*see 7.6.6*), the amount of alumina may be calculated.

7.11 Separation of Platinum and Manganese

7.11.1 Adjust the filtrate from the separation of the iron group (*see 7.6.5*) to about 300 ml by evaporation or dilution with water as necessary. Add 3 ml of concentrated hydrochloric acid and heat to incipient boiling. Pass through the liquid a stream of hydrogen sulphide at the rate of 5 to 10 bubbles per second for 20 min, while maintaining this temperature. Filter the solution hot through a fine filter paper and wash the precipitate four times with water containing hydrogen sulphide. Incinerate the filter paper and precipitate in a platinum, silica or porcelain crucible by gently beating, burning off the last traces of carbon at about 800 °C. Treat the residue with 2 ml of boiling, concentrated hydrochloric acid, dilute to 10 ml and filter through a fine filter paper into the main filtrate. Discard the precipitate which is due to platinum contributed by the laboratory apparatus.

7.11.2 Cool the combined filtrates to room temperature and add 6 ml of concentrated ammonium hydroxide solution. Transfer the liquid to a flask just large enough to contain it and pass hydrogen sulphide at the rate of 5 to 10 bubbles per second for 10 min. Add 2 ml of concentrated ammonium hydroxide solution, cork the flask and allow to stand overnight. Filter the liquid through a fine filter paper, washing the precipitate four times with water containing a trace of ammonium chloride and hydrogen sulphide. Discard the precipitate which is due to manganese.

7.11.3 Add a slight excess of concentrated hydrochloric acid to the filtrate and boil until there is no smell of hydrogen sulphide. Add 10 ml of bromine water and boil until the bromine colour has gone. If a precipitate is formed, filter and extract the residue as preciously described under **7.11.1**. Discard the precipitate. The filtrate is in a suitable state for the determination of calcium oxide (*see 7.12*).

7.12 Determination of Calcium Oxide

7.12.1 Heat the nitrate obtained in **7.11.3** to boiling and, while stirring, add 40 ml of hot saturated ammonium oxalate solution followed by concentrated ammonium hydroxide solution drop by drop until there is an excess. Continue boiling for 5 min to 10 min and allow to stand for a minimum period of 4 h, or until the precipitate has settled completely. Decant the clear liquid through a fine filter paper without transferring the precipitate. Remove the beaker containing the filtrate and replace with the one containing precipitate. Reserve the filtrate.

7.12.2 Wash the filter paper five times with 10 ml of hot, dilute, hydrochloric acid followed by one washing with water. Dilute the solution to 300 ml, boil and add 5 ml of hot saturated ammonium oxalate solution and a slight excess of ammonium hydroxide, stirring during the additions. Allow to stand for a minimum period of 4 h as under **7.12.1**.

7.12.3 Filter the liquid through a fine filter paper or preferably through asbestos in a gooch crucible. Transfer the precipitate to the filter, wash five times with dilute ammonium oxalate solution and then five times with 5 ml portions of warm water. Combine the filtrate and washing with those under **7.12.1** and reserve.

NOTE — Asbestos in a gooch crucible with a detachable base is the best filtering medium. It is quicker than filter paper and the washing of precipitate is more thorough.

7.12.4 Transfer the precipitate into a beaker using 100 ml of warm, weak sulphuric acid. If asbestos has been used, transfer the whole contents of the crucible to the beaker; if filter paper has been used make a small hole in the apex of the cone with a thin glass rod and rinse the precipitate into the beaker with the sulphuric acid. Warm the solution to about 70 °C and titrate with a decinormal solution of potassium permanganate. If filter paper has been used, drop the paper into the solution and complete the titration. Calculate on the basis that 1 ml of decinormal solution of potassium permanganate is equivalent to 0.002 804 g of calcium oxide (CaO).

7.13 Determination of Magnesium Oxide

7.13.1 Acidify the combined filtrates reserved in **7.12.3** by the addition of a slight excess of dilute hydrochloric acid. Stir briskly with a rubber tipped glass rod, taking care that it does not touch the sides. While stirring, add an excess of sodium phosphate solution followed by an amount of concentrated ammonium hydroxide solution equal to one-fifth of the volume of the solution. Allow the liquid to stand overnight.

7.13.2 Filter through a fine filter paper without transferring the precipitate. Discard the filtrate and replace with the beaker used in the precipitation. Wash the filter paper five times with hot, dilute hydrochloric acid. Dilute the solution to 200 ml and re-precipitate but using only 5 ml of a solution of sodium phosphate and 30 ml of ammonium hydroxide. Allow to stand for a minimum period of 5 h or longer if necessary to obtain a clear supernatant liquid.

7.13.3 Filter through a fine, low-ash, filter paper transferring the precipitate to the paper. Wash five times with cold, weak ammonium hydroxide solution. Discard the filtrate. Dry the paper and precipitate in an oven at 100 °C to 105 °C.

7.13.4 Separate the precipitate from the filter paper as completely as possible and transfer the paper to a weighed platinum or silica crucible. Char the paper without flaming, finally removing the residual carbon at a bright-red heat. Cool, add the precipitate, heat slowly to 1 000 °C to 1 050 °C and maintain at this temperature for 20 min. Cool in a desiccator and weigh. Repeat the heat treatment in 5 min periods to constant mass. Calculate the mass of magnesium oxide (MgO) using the relation that 1 g of the above precipitate corresponds to 0.362 1 g of magnesium oxide.

7.14 Determination of Oxide of Manganese

Boil 1 g of ash accurately weighed with 15 ml of sulphuric acid (1:1) for 5 min, allow to cool and add 50 ml of dilute nitric acid. Heat the solution to boiling, cool to 15 °C and add slowly 3 g of sodium bismuthate with continuous agitation. Add 50 ml of weak nitric acid, and filter through a thin layer of asbestos using a Hirsch funnel. Wash with 80 ml of weak nitric acid. Discard the residue. Add a measured excess of a decinormal solution of ferrous ammonium sulphate to the combined filtrate and washings and titrate the excess ferrous iron present with potassium permanganate solution. Calculate on the basis that 0.001 525 g of the oxide of manganese (Mn₃O₄) is equivalent to 1 ml of decinormal ferrous ammonium sulphate solution.

7.15 Phosphorus in Ash of Coal and Coke

7.15.1 General

Besides carbon, hydrogen, nitrogen and sulphur, which occur in all coals and cokes in appreciable quantities, it is sometimes necessary also to determine the percentage of phosphorus, chlorine and arsenic which are present in smaller quantities. The determination for chlorine and arsenic are made on the material taken from the analysis sample of 0.5 kg of air-dried coal ground to pass IS sieve 20 (211 microns). The phosphorus is usually determined in the ash.

7.15.2 General Outline

- a) There are two methods, one gravimetric (phosphomolybdate) and the other volumetric. In the gravimetric method a known mass of the ash is heated with a mixture of hydrofluoric and nitric acids to remove silica which escapes as silicon tetrafluoride. Alternatively, a known mass of the ash is fused with a mixture of potassium and sodium carbonate. The fused mass is extracted with dilute nitric acid and the silica removed by filtering.
- b) The phosphoric acid in the aqueous extract is precipitated as phosphomolybdate which is then weighed to determine the percentage by mass of phosphorus. From the value of ash determined as prescribed under **9** of IS 1350 (Part 1), the results now obtained, the percentage of phosphorus in the air-dried prepared sample is calculated.
- c) Errors due to the presence of arsenic in the amount normally present in coal are insignificant. The inhibiting effect of titanium is reduced to negligible proportions by the strength of the nitric acid used. In the cases where the interference due to arsenic is believed to be significant, the following precautions may be taken:
 - i. The coal ash may be digested with a mixture containing ferric chloride, hydrochloric acid and hydrogen bromide to expel the arsenic as the volatile arsenious chloride.
 - ii. The phosphomolybdate precipitation may be carried out at 50 °C.

7.15.3 Determination of Phosphorus by the Gravimetric (Phosphomolybdate) Method

7.15.3.1 Apparatus

7.15.3.1.1 Crucibles, two; one of platinum, of 30 ml capacity, with lid, for alkaline fusion method and the other of sintered glass (No. 3).

7.15.3.2 Reagents

7.15.3.2.1 Concentrated Nitric Acid, specific gravity of 1.42 (*see* IS 264)

7.15.3.2.2 *Nitric Acid*, specific gravity of 1.20, prepared by diluting 390 ml of concentrated nitric acid with water to 1 litre.

7.15.3.2.3 *Dilute Nitric Acid*, 2.5 percent by volume obtained by diluting one volume of concentrated nitric acid with water to four volumes.

7.15.3.2.4 *Weak Nitric Acid*, obtained by diluting 1.5 volumes of concentrated nitric acid with water to 100 volumes.

7.15.3.2.5 *Hydrofluoric Acid*, a solution in water containing about 550 g of hydrogen fluoride per litre and free from phosphorus.

7.15.3.2.6 *Fusion Mixture*, containing three parts of anhydrous sodium carbonate and two parts of anhydrous potassium carbonate.

7.15.3.2.7 *Concentrated Hydrochloric Acid*, specific gravity of 1.16 (*see* IS 265)

7.15.3.2.8 *Phenolphthalein Indicator*, prepared by dissolving 1 g phenolphthalein in 80 ml of ethyl alcohol and diluting with water to 100 ml, then filtering.

7.15.3.2.9 *Sodium Hydroxide Solution*, approximately 0.1 N

7.15.3.2.10 *Concentrated Ammonium Hydroxide Solution*, specific gravity of 0.90

7.15.3.2.11 *Dilute Ammonium Hydroxide Solution*, approximately 4.5 N prepared by adding one volume of concentrated ammonium hydroxide solution to two volumes of water.

7.15.3.2.12 *Ammonium Molybdate Solution*, *see* **7.2.38**

7.15.3.2.13 *Potassium Nitrate*, solid

7.15.3.2.14 *Dilute Ammonium Nitrate Solution*, containing 3 g of ammonium nitrate and 1.5 ml of dilute nitric acid (specific gravity of 1.20) dissolved in 100 ml of water.

7.15.3.2.15 *Concentrated Ammonium Nitrate Solution*, 50 percent (m/v)

7.15.3.2.16 *Ethyl Alcohol*, 95 percent (by volume) rectified spirit conforming to IS 323

7.15.3.2.17 *Absolute Alcohol*, *see* IS 321

7.15.3.3 Procedure

In the following method it is assumed that all the phosphorus has been retained in the ash. The various stages of the procedure are described below:

a) *Preparation of Extract* — An extract of the ash is prepared by one of the following techniques.

i) *Extraction with a mixture of nitric acid and hydrofluoric acid*

Grind the ash in an agate mortar to an impalpable powder all passing through IS Sieve 6 (64 microns). Carry out a preliminary determination using 0.5 g of ash and depending upon the phosphorus content and weigh out the appropriate quantity of the ash into a platinum crucible of about 30 ml capacity as follows:

<i>Phosphorus Content of Ash</i>	<i>Mass, in g, of Ash to be Taken</i>
Less than 0.1	1.0
0.1 to 0.25	0.5
0.25 to 0.5	0.4
0.5 to 0.75	0.25
0.75 to 1.0	0.2
Greater than 1.0	0.1

Add carefully 10 ml of concentrated nitric acid and 5 ml of hydrofluoric acid and cautiously evaporate to dryness during a period of about 45 min, preferably on a hot plate or a hot sand bath for which the sand has been extracted previously with acid. Add further 10 ml of concentrated nitric acid and 5 ml of hydrofluoric acid, digest and evaporate to dryness as before. To ensure complete removal of the hydrofluoric acid, add further 5 ml of concentrated nitric acid and again evaporate to dryness. Carry out all evaporations, with the crucible partly covered with the lid in order to avoid error due to accidental 'spitting'. Do not ignite at any stage. Add 15 ml of nitric acid (specific gravity of 1.20) to the crucible and evaporate the contents to about 7 ml. Transfer the solution to a 250 ml beaker and wash the crucible with water, adding the washings to the contents of the beaker. The combined volume of the washings and the original solution should be about 80 ml. Cover the beaker with a clock glass and boil the contents of the beaker for 15 min, allowing a glass rod to stand in it to inhibit bumping.

ii) *Fusion with a mixture of sodium and potassium carbonate*

Weigh accurately into the platinum crucible a suitable quantity of ground ash [see 7.15.2 (c)(i)] and mix intimately with 3 g of fusion mixture. Cover the contents with a layer of 1 g of the fusion mixture and fuse at 700 °C to 800 °C. When cold, place the crucible in an evaporating basin, cover with distilled water and add 15 ml of concentrated hydrochloric acid. When the melt has dissolved, remove the crucible and wash it out with distilled water adding the washing to the solution in the basin. Add 5 ml of concentrated nitric acid, evaporate to dryness and bake on a hot plate for 1 h. Allow to cool, add 5 ml of concentrated nitric acid and 50 ml of distilled water and heat the solution to boiling.

b) *Filtration of extract obtained by either method*

Filter the extract through a thick, general purpose, fine filtering, 9 cm diameter filter paper (Whatman No. 3), into a 400 ml beaker and wash the filter paper with water, collecting the washings until they are free from acid, that is until 10 ml of the final washings, give an alkaline

reaction with one drop of phenolphthalein and one drop of sodium hydroxide solution. The final volume of the filtrate should be about 250 ml.

c) Precipitation

Evaporate the solution to about 50 ml. Add concentrated ammonium hydroxide solution carefully, drop by drop, with continual rotation of the contents of the beaker until a slight permanent precipitate of iron and aluminum hydroxides appears. Redissolve this precipitate by addition of the minimum quantity of concentrated nitric acid keeping the contents of the beaker agitated, and finally add 4 ml excess of concentrated nitric acid and add 3 g to 4 g of potassium nitrate. The volume of the liquid should not now exceed 70 ml. Heat the contents of the beaker to 75 °C, and slowly add 30 ml of ammonium molybdate solution, previously heated to 55 °C, in a thin stream, with constant agitation of the liquid. Maintain at 50 °C for 30 min. Keep the beaker containing the phosphomolybdate precipitate, with occasional stirring for 2.5 h at room temperature (25 °C to 30 °C), allow it to settle and then filter through a medium filtering, 9 cm diameter filter paper, retaining as much of the precipitate as possible in the beaker. Wash the precipitate in the beaker twice, each time with 30 ml of the wash liquid (dilute ammonium nitrate solution).

d) Re-precipitation

Dissolve the precipitate on the filter paper with 10 ml of dilute ammonium hydroxide solution, delivered from a pipette, and wash the paper with water 5 times, using 10 ml each time, the total volume of the liquid not exceeding 60 ml. Dissolve the major part of the phosphomolybdate precipitate (in the beaker) in 10 ml of dilute ammonium hydroxide solution and add to this solution, the solution of the precipitate from the filter paper and the washings. Next, add 10 ml of concentrated ammonium nitrate solution and 1 ml of ammonium hydroxide solution and heat the mixture to 55 °C to 60 °C. Pour, in a thin stream into the middle of the beaker 30 ml of dilute nitric acid previously warmed to 70 °C. Rotate the liquid during the addition of the dilute nitric acid, and for 2 min to 3 min afterwards. After 15 min, filter the precipitate through the weighed sintered-glass crucible. Wash the phosphomolybdate 4 times with weak nitric acid using 15 ml each time, twice with dilute ammonium nitrate solution using 15 ml each time, twice with water, using 5 ml each time, and finally, 3 times with absolute alcohol, using 3 ml each time. Dry at 125 °C to 130 °C in the oven for 30 min and cool in a freshly charged desiccator containing concentrated sulphuric acid. Repeat till the mass is constant.

7.15.3.4 Calculation

Calculate the phosphorus content of the ash on the basis that 1 g of ammonium phosphomolybdate is equivalent to 0.016 5 of phosphorus.

7.16 Determination of Alkalis

7.16.1 General

Two methods (Method A and Method B) have been prescribed for the determination of alkalis.

7.16.2 Method A

7.16.2.1 Important Precaution

It is extremely important that specially prepared reagents, as free as possible, from alkali metals should be used.

7.16.2.2 Mix 0.8 g of bulk ash (*see* **6.4.3**), accurately weighed, with 0.8 g of ammonium chloride and 6 g of precipitated calcium carbonate by grinding together in an agate mortar. Transfer the mixture to a platinum crucible fitted with a lid, a little calcium carbonate having been placed previously at the bottom of the crucible. Place the crucible in a suitable shield of asbestos-cement board so arranged that only the lower half of the crucible is directly heated. Heat gently until ammonia ceases to evolve, then raise the temperature to about 700 °C (dull-red heat), maintaining at this temperature for 75 min.

7.16.2.3 Shake the cooled sintered mass with about 5 ml of water, transfer the contents of the crucible to a beaker and digest with 50 ml of hot water. Allow to settle and decant the supernatant liquid through a fine filter paper. Repeat the digestion and decantation twice, finally transferring the residue to the filter paper. Wash with hot water. Discard the residue.

7.16.2.4 Precipitate any sulphate present in the combined filtrates by the addition, in the normal manner, of barium chloride solution, slightly acidified with hydrochloric acid. Filter through a fine filter paper and discard the residue.

7.16.2.5 Treat the filtrate successively with slight excesses of both concentrated ammonium hydroxide solution and ammonium carbonate solution. Filter through a fine filter paper, redissolve the precipitate in dilute hydrochloric acid, and repeat the precipitation and filtration. Discard the residue. Evaporate the combined filtrate to dryness in a platinum basin and remove ammonium salts by careful baking in a muffle furnace at 450 °C.

7.16.2.6 Rinse down the sides of the basin with 25 ml of hot water. Add dilute barium chloride solution drop by drop, until one drop causes no further precipitation. Add 1 ml of dilute ammonium oxalate solution, followed by 2 ml of ammonium carbonate solution and one drop of concentrated ammonium hydroxide solution. Allow the mixture to stand for at least 4 h, preferably overnight.

7.16.2.7 Filter through a small, fine, filter paper into a platinum basin washing the precipitate three times with water. Discard the precipitate. Evaporate the filtrate to dryness and remove the ammonium salts as described under **7.16.5**. Extract the baked residue with 5 ml to 10 ml of hot water and filter through a small, fine, filter paper into a weighed platinum basin, washing the paper six times with hot water. Discard the residue. Add 10 drops of concentrated hydrochloric acid to the filtrate and evaporate the mixture to dryness. Heat in a muffle furnace at 450 °C. Cool in a desiccator and reweigh. The increase in the mass is the mass of mixed alkali chlorides present.

7.16.2.8 Dissolve the mixed chlorides in about 5 ml of water and transfer to a small evaporating basin of good quality glass. Add 2 ml of perchloric acid (*see* **6.5.3**) and gently evaporate to dryness

on a hot plate which is not above 350 °C. Cool, add 5 ml of water and evaporate to dryness as before.

7.16.2.9 Dry a 50 ml conical flask and a filter stick and weigh together. Remove the filter stick temporarily to a desiccator or stoppered tube. Transfer the dried residue from the evaporating basin to the conical flask by successive rinsings with 2 ml of hot water. Evaporate to dryness in the flask, finishing in an oven for 1 h at about 110 °C. Cool in a desiccator. Add 5 ml of pure ethyl acetate or absolute alcohol saturated with potassium perchlorate, cork the flask and swirl the liquids around gently for 5 min. Remove the cork, connect the filter stick to a suction pump and insert it into the solution. Insert a strap between the filter stick and the pump to catch the filtrate. Take as much as possible of the solution through the filter stick. Wash down the inside of the flask and the outside of the filter stick with four separate portions of 5 ml of ethyl acetate, with drawing each separate portions through the filter stick. With suction, still applied, immerse the lower portion of the flask in hot water and draw out the vapour of ethyl acetate. Detach the filter stick and again dry the flask and stick at 110 °C to constant mass.

7.16.2.10 *Calculation*

The increase in mass is potassium perchlorate. For extreme accuracy and to correct for the amount dissolved by the ethyl acetate, add 0.000 3 g to the mass of potassium perchlorate found. Calculate the alkali content on the following basis:

- a) 1 g of potassium perchlorate is equivalent to 0.538 1 g of potassium chloride (KCl),
- b) 1 g of potassium chloride is equivalent to 0.631 4 g of potassium oxide (K₂O), and
- c) 1 g of sodium chloride is equivalent to 0.530 g of sodium oxide (Na₂O).

7.16.3 Method B

7.16.3.1 *General*

Determination of alkalis by this method shall be carried out using flame photometer.

7.16.3.2 *Preparation of Coal/Coke Ash*

Prepare 3 g to 5 g of ash from thoroughly mixed air-dried coal or coke which has been ground to pass 212-microns sieve. Spread the coal or coke in a layer not over 6 mm in depth in a fireclay or porcelain roasting dish. Place in a cold muffle furnace and heat gradually to a temperature of 500 °C in 1 h and (815 ± 10) °C in 2 h. Allow the ash to cool, transfer, agate, and store for analysis. Thoroughly mix each sample before weighing. If stored, reignite before weighing. If difficulty in ashing is encountered for coke, may be ignited at (900 ± 50) °C.

7.16.3.3 *Apparatus*

7.16.3.3.1 *Balance*, sensitive to 0.1 mg

7.16.3.3.2 Crucible, platinum basins, 100 ml capacity, shall be used for decomposition of the ash with HF.

7.16.3.3.3 Flame Photometer

7.16.3.3.4 Muffle Furnace, electrically-heated muffle furnace with good air circulation and capable of maintaining a temperature of approximately 1 000 °C.

NOTE — Analytical grade reagents shall be used. Unless otherwise indicated, all reagents to be of high purity permit its use without lessening the accuracy of the determination. Water to be used shall be double distilled and free from Na⁺ or K⁺ radicals.

7.16.3.4 Reagents

7.16.3.4.1 Concentrated Hydrochloric Acid, specific gravity 1.18

7.16.3.4.2 Hydrofluoric Acid, specific gravity 1.15

7.16.3.4.3 Perchloric Acid, about 70 percent, specific gravity 1.67

7.16.3.4.4 Preparation of Stock Solution

a) *Potassium, Concentrated Stock Solution (100 ppm)*

Dissolve 0.190 70 g of potassium chloride (KCl) / 0.258 6 g of potassium nitrate (KNO₃) or 0.222 8 g of potassium sulfate (K₂SO₄) in water and dilute to 1 000 cm³.

b) *Sodium, Concentrated Stock Solution (100 ppm)*

Dissolve 0.251 6 g of sodium chloride (NaCl) / 0.308 8 g of sodium sulphate (Na₂SO₄) in water and dilute to 1 000 cm³.

c) *Preparation of Synthetic Ash Solution*

- i. Dissolve 1.0 g of aluminum in 10 cm³ of sulphuric acid (H₂SO₄) and add 100 cm³ of water;
- ii. Dissolve 2.0 g of iron in 10 cm³ of sulphuric acid (H₂SO₄) (1 : 1) and add 100 cm³ of water;
- iii. Dissolve 1.25 g of CaCO₃ in 3 cm³ of sulphuric acid (H₂SO₄) (1 : 1) and about 6 000 cm³ of water is added to it; and
- iv. Dissolve 1 g of magnesium sulphate (MgSO₄) in water. Combine all solution, filter and dilute to 1 000 cm³.

d) *Preparation of Standard Solution*

To prepare different ppm level (10, 20, 40 or 1) standard solution of sodium and potassium, pipette (10, 20, 40 or 1) ppm of sodium or potassium from stock solution into a 100 cm³ volumetric flask. Add 10 cm³ of synthetic ash solution and 10 cm³ of sodium or potassium (that is if sodium standard is prepared, add 10 cm³ of potassium stock solution or *vice versa*) dilute with water to the mark and mix, store in plastic bottle.

7.16.3.5 *Dissolution of Sample*

To dissolve, grind a representative sample of ash to pass through 100 mesh sieve and remix thoroughly. Place 0.1 g of sample in a 100 cm³ platinum basin, add 5 cm³ of HF; 3 cm³ of HNO₃; and 2 cm³ of HClO₄ and digested to dryness. Repeat the process. Once dried add 2 cm³ of HClO₄ and evaporate to dryness. Add few drops of HClO₄ or HCl to moisten the mass and add 20 ml distilled water and evaporate the same to 1/2 of its volume. Transfer the same solution by filtering and make the volume to 250 ml in a volumetric flask. Take aliquot solution to aspirate for determination of alkalies.

7.16.3.6 *Calibration*

After adjusting the flame spectrophotometer according to the manufacturer's direction, set the wavelength to 589 nm and aspirate sodium solution of different ppm level and determine the transmittance reading. Repeat this operation for checking the transmittance. Test the blank solution and make similar measurements for the standard potassium solution at a wavelength of 766 nm and plot the data obtained.

7.16.3.7 *Procedure*

Set the instrument as has been done while calibration. Rinse a sample cup with the solution it is to contain and fill separate cups with standard solution of required ppm level. Adjust instrument according to the range of standard. Make the readings of sample solution and blank solution. Subtract the blank reading from the sample readings and determine the concentration of sodium and potassium in the test solution from the appropriate working curve.

7.16.3.8 *Calculation*

Calculate the percent sodium oxide and potassium oxide as follows:

a) Sodium oxide (Na₂O), percent = $X_{Na} \times 0.3375$

where

X_{Na} = amount of sodium, in ppm, when 0.1 g of sample is taken in 250 cm³ solution.

If $X_{Na} = 1$ ppm, then the sodium oxide percent contained in 250 cm³ which originally came from 0.1 g ash is 0.000 337 5 g, that is, 0.337 percent.

b) Potassium oxide (K₂O), percent = $X_K \times 0.301\ 25$

where

X_K = amount of potassium, in ppm, when 0.1 g of sample taken in 250 cm³ solution.

If $X_K = 1$ ppm, then the potassium oxide percent contained in 250 ml which originally came from 0.1 g ash is 0.000 301 25 g, that is, 0.301 percent.

7.16.3.9 Conversion calculation from ppm to percentage (100 units in digital display is equivalent to 10 ppm)

a) $4Na + O_2 \rightarrow 2 Na_2O$, that is, $Na = 1/2 Na_2O$

Hence conversion factor from Na to Na₂O is 1.35.

So, ppm to percent conversion is:

If X , ppm = experimental value after deduction of blank value, then X , ppm $\times 1.35 \times 1/0.1 \times 1/10^6 \times 100 \times 250 = X$, ppm $\times 0.337\ 5$ (when 0.1 g sample is taken, and volume made up to 250 ml).

b) $4K + O_2 \rightarrow 2K_2O$

$K = 1/2 K_2O$

Hence the conversion factor from K to K₂O is 1.205.

So, ppm to percent conversion:

If X , ppm = experimental value after deduction of blank value, then X , ppm $\times 1.205 \times 1/0.1 \times 1/10^6 \times 100 \times 250 = X$, ppm $\times 0.301\ 5$ (when 0.1 g sample is taken and volume made up to 250 ml).

NOTE — The method is applicable for total Na₂O, K₂O content. It shall also be applied to both water soluble, as well as acid soluble alkalis.

- i. *Water Soluble Alkali* — After suitable extraction with water, the extract after filtration and marking volume 250 ml, the same procedure may be adopted for the said solution.
- ii. *Acid Soluble Alkali* — After suitable extraction with desired acid, the extract after filtration and making volume 250 ml, the same procedure may be adopted for the said solution.

7.17 Determination of Sulphur

7.17.1 The determination of sulphur (as trioxide) shall be carried out on standard ash.

7.17.2 Treat an accurately known mass (usually about 0.5 g) of standard ash with 5 ml of bromine water and 100 ml of dilute hydrochloric acid and boil for 1 h. Filter through a fine filter paper and wash the insoluble residue with hot water. Reserve the residue. Neutralize the filtrate with concentrated ammonium hydroxide solution and add 2 ml of concentrated hydrochloric acid. Make up the volume to about 250 ml. Boil the solution, and, while boiling, treat it with 15 ml of concentrated barium chloride solution, added drop by drop, to permit uninterrupted boiling. Continue boiling for a further 15 min and allow to stand for a minimum period of 4 h in a sulphur-free atmosphere and protected from dust.

7.17.3 Filter, using one of the following techniques:

7.17.3.1 By gravity, through an ashless fine-textured double acid-washed filter paper in a fluted, long-stemmed, 60° funnel, the filter-circle being carefully folded to fit the funnel so that the stem remains full of liquid.

or

7.17.3.2 By gravity, through a filter-paper pad prepared from ashless double acid-washed filter paper (*see* Note).

NOTE — For preparing the filter-paper pad, shake double acid-washed filter-paper clippings, in pieces of approximately 1 sq cm area, with distilled water in a bottle until the paper is thoroughly disintegrated. Place a 25 mm porcelain filter cone in a 75 mm funnel close the stem of the funnel with a finger and add distilled water until the cone is immersed and the funnel stem is full. Shake on to the cone sufficient pulp to form a pad 5 mm thick and level it with a flat-ended glass rod. Allow the excess water to drain away by removing the finger from the funnel stem and lightly tamp the pad round the edges with the glass rod as drain age ceases. Wash finally with distilled water.

or

7.17.3.3 Under suction, using good quality asbestos in a Gooch crucible which has been dried for 1 h at (130 ± 10) °C and weighed.

7.17.4 Wash the filter with hot distilled water, using not more than 250 ml, until 20 ml of the washings give not more than a faint opalescence with silver nitrate solution. Place wet filter paper in an ignited and weighed silica or platinum capsule on a silica plate and insert into the muffle furnace for 15 min at (800 ± 25) °C. If a filter pad is used, transfer the pad to the silica capsule, wipe the funnel successively with two halves of a circle of ashless filter paper and incinerate these with the pad. If a Gooch crucible is used, dry it for 1 h at (130 ± 10) °C. Cool and weigh.

7.17.4.1 Ignition is achieved rapidly with wet paper or pad and mechanical loss is avoided by the use of thick silica plate. If filter paper is used, the ignited residue shall be oxidized by the addition of a few drops of concentrated sulphuric acid and again heated and cooled before weighing, but this is seldom necessary.

7.17.5 Carry out a blank determination under the same conditions but omitting the coal-ash. Pipette 10 ml of the potassium sulphate solution to the filtrate after extraction. Deduct the mass of the barium sulphate found in the blank determination, less the barium sulphate equivalent of the potassium sulphate added, from the mass obtained in full determination.

7.17.6 1 g of barium sulphate is equivalent to 0.343 1 g of sulphur trioxide (SO₃). If the sulphur trioxide content is less than 5 percent, the determination may be considered to be concluded. If it is higher than 5 percent, transfer the filter paper and the residue (*see 7.17.2*) to a platinum crucible and burn off the paper by smouldering finally removing the residual carbon at a bright-red heat. Allow to cool and add 5 drops of concentrated nitric acid followed by 10 drops of hydrofluoric acid. Place the lid on the crucible and heat gently to drive off the acid. Slowly raise the temperature to 800 °C and allow it to cool. Repeat the acid treatment using 5 drops of each acid.

7.17.7 To the cooled residue add 1 g of sodium carbonate and heat to fusion for about 30 min. Dissolve the melt in 100 ml of boiling water containing a slight excess of hydrochloric acid. Filter through a fine filter paper. Discard the residue. Determine the sulphate present in the filtrate by precipitation with barium chloride as previously described. Add the amount of sulphate to that already obtained to account for the total sulphate present.

8 ALTERNATIVE METHOD

8.1 Apparatus

8.1.1 Silica Dish

8.1.2 Porcelain Basins, glazed, of 250 ml to 300 ml capacity

8.1.3 Platinum Crucible, of 30 ml or 40 ml capacity

8.1.4 Colorimeter

8.1.4.1 EEL Colorimeter is suitable.

8.1.5 Lawrence Smith Crucible, platinum

8.1.6 Platinum Basins, of 100 ml capacity

8.2 Reagents

8.2.1 Sodium Carbonate, anhydrous

8.2.2 Concentrated Hydrochloric Acid, specific gravity of 1.16 (*see IS 265*)

8.2.3 Dilute Hydrochloric Acid, 1.1 by volume

8.2.4 Hydrogen Peroxide Solution, 3 percent (*m/v*) or '10 volume' solution

8.2.5 Concentrated Sulphuric Acid, specific gravity of 1.84 (*see* IS 266)

8.2.6 Dilute Sulphuric Acid, 4 N, one volume of concentrated sulphuric acid diluted with eight volumes of water.

8.2.7 Hydrofluoric Acid, 38 percent to 40 percent (*m/v*)

8.2.8 Methyl Red Indicator Solution

Dissolve 0.5 g of the reagent in 300 ml of rectified spirit (*see* IS 323) and dilute with 200 ml of distilled water.

8.2.9 Ammonium Chloride, solid

8.2.10 Ammonium Hydroxide Solution, specific gravity of 0.90

8.2.11 Dilute Ammonium Hydroxide Solution, one volume of ammonium hydroxide solution diluted with seven volumes of water.

8.2.12 Ammonium Nitrate Solution, 2 percent (*m/v*)

8.2.13 Ammonium Thiocyanate Solution, 60 percent (*m/v*)

8.2.14 Standard Mercurous Nitrate Solution

Dissolve about 30 g of mercurous nitrate ($\text{HgNO}_3 \cdot \text{H}_2\text{O}$) in 100 ml of 5 percent (*m/v*) nitric acid. Oxides of nitrogen should be removed from the nitric acid, by adding urea, otherwise, oxides of nitrogen give blood-red coloured nitrosyl thiocyanate complex with ammonium thiocyanate standardize as prescribed under **7.2.21.1**.

8.2.15 Standard Titania Solution

Fuse 0.5 g of titanium dioxide (TiO_2) with 2.5 g of potassium pyrosulphate, dissolve the melt in 25 ml of dilute sulphuric acid and make up the volume to 500 ml.

8.2.16 Phosphoric Acid, 85 percent (*m/v*)

8.2.17 Ammonium Oxalate Solution, saturated

8.2.18 Standard Potassium Permanganate Solution, approximately 0.1 N

8.2.19 Concentrated Nitric Acid, specific gravity of 1.42 (*see* IS 264)

8.2.20 Diammonium Hydrogen Phosphate Solution, 10 percent (*m/v*)

8.2.21 Calcium Carbonate

Precipitated, free from alkali as far as possible.

8.2.22 Ammonium Carbonate Solution, 10 percent (m/v)

8.2.23 Concentrated Barium Chloride Solution, containing 100 g of pure crystalline barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) per litre.

8.2.24 Dilute Barium Chloride Solution, one volume of the concentrated solution, diluted to ten volumes with water.

8.2.25 Zinc Uranyl Acetate Solution

The solution is made by mixing equal volumes of solution A and solution B.

a) *Solution A* — Mix 10 g of uranyl acetate [$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$] with 3 ml of glacial acetic acid and 50 ml of water, warm until the solid is dissolved and then filter.

b) *Solution B* — Mix 30 g of zinc acetate ($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$) with 2 ml of glacial acetic acid and 50 ml of water, warm until the solid is dissolved and then filter.

8.2.26 Extracing Alcohol

Rectified spirit (*see* IS 323) saturated with sodium zinc uranyl acetate for washing precipitate from sodium.

8.2.27 Bromine Water, saturated

8.2.28 Potassium Pyrosulphate, solid

8.2.29 Sodium Sulphate, solid

8.2.30 Glacial Acetic Acid

8.2.31 Potassium Nitrate Solution, 0.1 percent (m/v)

8.3 Preparation of Ash

The ash is prepared as described under **7.3** or **7.4**. For complete analysis in duplicate 5 g to 8 g of bulk ash are required. The ash as made under **7.4** absorbs moisture and carbon dioxide during grinding. Before carrying out the analysis, the ground ash is therefore heated in a silica dish at a temperature of $(815 \pm 10)^\circ\text{C}$ for about 30 min. Analysis should be carried out in duplicate.

8.4 Procedure

8.4.1 The first stage covers the fusion of ash with sodium carbonate. The method for ash low in iron content is different from the method for ash high in iron content.

8.4.1.1 *For ash low in iron*

Accurately weigh about 0.5 g of ash in a platinum crucible acid mix thoroughly with 3 g of sodium carbonate using a clean glass rod. Brush into the crucible with a camel hair brush any particles adhering to the rod. Sprinkle one gram of sodium carbonate over the mixture and fuse as described under **8.4.1.3**.

8.4.1.2 *For ash high in iron*

If the ash contains much iron, as will be evident from the colour, extraction with concentrated hydrochloric acid should precede the fusion of the residue. For this digest about 0.5 g of the ash, accurately weighed, with 10 ml of concentrated hydrochloric acid in a porcelain basin, fitted with a cover-glass, on a steam-bath until only half the acid remains. Repeat the operation with a further 5 ml portion of acid. Digest the mass with about 50 ml of hot water for about 15 min. Filter through a filter paper (Whatman No. 42) into a porcelain basin. Wash the residue 5 to 6 times with hot water, collecting the washings with the main filtrate. Reserve the filtrate [*see 8.4.2.1*]. Transfer the residue with its filter paper to a platinum crucible and dry with slow heat. Finally, incinerate at a dull-red heat to remove carbonaceous matter which can best be removed by tilting the crucible, and placing the lid across the width of the crucible. Mix the non-carbonaceous residue with 3 g of sodium carbonate as described in **8.4.1.1** and fuse as described under **8.4.1.3**.

8.4.1.3 *Fusion*

Cover the crucible with the lid and raise the heat slowly. After a few minutes, raise the temperature until fusion takes place. Maintain fusion for about half an hour, care being taken to prevent boiling of excessive turbulence of the melt. Avoid admitting reducing gases into the crucible, otherwise a black stain may develop on the platinum surface due to reaction of iron with platinum forming iron platinum alloy (*see 7.5.3*).

8.4.2 *Determination of Silica*

8.4.2.1 Remove the crucible from the flame and swirl it so that the melt spreads on the sides. Cool, add 15 ml of hot water to the melt and put the crucible with the lid in a porcelain basin. Add, slowly 20 ml of dilute hydrochloric acid. Warm the solution to hasten decomposition of mass. Wash the sides with hot water. Add two drops of hydrogen peroxide to decompose any manganate. Remove the crucible and the lid, and wash both into the basin with hot water. In case the ash had been subjected to the preliminary treatment of digestion with hydrochloric acid, mix the filtrate [*see 8.4.1.2*] with the liquid in the porcelain basin. Place the porcelain basin either on a water-bath or on a sand bath for evaporation, a cover-glass being placed over a glass triangle above the basin to eliminate contamination by dust.

8.4.2.2 After evaporation, cool the basin. Grind the mass with a glass rod, one end of which has been flattened for the purpose. Place the basin with the cover-glass and glass rod in an air-oven

maintained at a temperature of 108 °C to 110 °C for about 2 h. Remove the porcelain basin from the oven, cool, moisten the mass with 5 ml of concentrated hydrochloric acid, then add 25 ml of hot water and digest for 5 min to 10 min on a water-bath. Filter through a rapid, low-ash filter paper (Whatman No. 40). Wash the residue with hot water until the filtrate is free from chloride and retain the precipitate. Evaporate the filtrate again on a water-bath and, when dry, grind the mass with a glass rod and then place in the air-oven for 2 h, grinding the mass once more during this heating. Remove the basin and allow it to cool. When cold, moisten the mass with 5 ml of concentrated hydrochloric acid, add 20 ml of hot water and digest as above. Filter, and wash the residue with hot water until the filtrate is free from chloride. Reserve the filtrate and the washing.

8.4.2.3 Put the precipitates from both the operations together with the filter papers into a weighed platinum crucible. Char the filter paper at a low heat, so that it does not catch fire, the lid being so placed on the crucible that easy access of air inside the crucible is ensured. Do not raise the heat until all the carbon has been burnt away, then heat up to 1 000 °C and maintain at this temperature for 40 min to 50 min. Cool in a sulphuric acid desiccator, weigh immediately, and repeat the ignition to constant mass. Moisten the residue with 4 drops of water and add 2 drops of concentrated sulphuric acid followed by about 5 ml of concentrated hydrofluoric acid. Place the crucible on a sand bath and heat slowly. When all the liquid has evaporated, add 5 ml of hydrofluoric acid and heat on a sand bath. At the last stage heat slowly to drive off the final traces of sulphuric acid. Heat the crucible at 1 000 °C for 5 min, cool, weigh and express the loss in mass as percentage of silica.

8.4.3 *Determination of Barium Oxide*

Fuse the residue in the platinum crucible with 0.5 g of sodium carbonate. Cool, and dissolve, the melt in 100 ml of water containing 1 ml of concentrated sulphuric acid, and digest the mass on water-bath for some time. The turbidity is due to barium sulphate. Digest the precipitate for at further 15 min, allow it to stand for 30 min, and then filter through a fine textured double acid-washed filter paper (Whatman No. 42) and keep the filtrate. Wash the precipitate 5 to 6 times with hot water, ignite the precipitate of barium sulphate in the usual manner (*see 7.17*) and weigh the barium sulphate. Report the result as percentage of barium oxide (BaO).

8.4.4 *Precipitation of Mixed Oxides*

8.4.4.1 Add the filtrate from silica separation [*see 8.4.2.2*]. Evaporate the mixed filtrates to volume of about 250 ml. To the incipient boiling solution add two drops of methyl red indicator. In case much iron is present (as judged from the colour of the solution) additions of the indicator is not necessary. Add 5 g of ammonium chloride followed by concentrated ammonium hydroxide solution with continuous stirring with a glass rod until a precipitate just appears. Add dilute ammonium hydroxide solution dropwise and test with methyl red indicator thread until the solution is just alkaline. Raise the temperature of the liquid to just boiling, remove immediately from the source of heat or keep the covered solution at a lower temperature for 5 min to 10 min and then allow to stand at room temperature until the precipitate has settled. Boiling makes the precipitate slimy which settles very slowly. Decant the supernatant liquid through a medium textured low-ash filter paper (Whatman No. 41) containing some finely macerated filter paper pulp. Removal of the

last traces of precipitate adhering to the sides of the beaker is not necessary. Wash the precipitate with warm ammonium nitrate solution 3 to 4 times.

8.4.4.2 Evaporate the filtrate to a small bulk and reserve it.

8.4.4.3 Take the precipitate together with the pulp in the original beaker in which precipitation was done. Add a few millilitres of dilute sulphuric acid and about 50 ml of water. All the precipitate will go into solution. Heat the solution to boiling with continuous stirring with a glass rod in order to avoid bumping, add 2 g to 3 g of ammonium chloride followed by dilute ammonium hydroxide solution to precipitate mixed oxides as described under **8.4.4.1**. Filter through a medium textured, low-ash filter paper (Whatman No. 41) taking care to transfer quantitatively the last traces of precipitation adhering to the sides of the beaker on to the filter paper by a rubber-tipped glass rod (policeman). Wash the precipitate with warm ammonium nitrate solution 5 to 6 times. Add the filtrate together with the washings to the filtrate from the first operation [*see 8.4.4.2*].

8.4.4.4 Dissolve the precipitate in 20 ml of dilute sulphuric acid and warm. When solution is complete, filter through a medium textured, low-ash filter paper (Whatman No. 41) to remove filter pulp, cool and, make up to 250 ml in a measuring flask.

8.4.5 *Analysis of the Mixed Oxide Precipitate*

8.4.5.1 *Determination of Iron Oxide*

8.4.5.1.1 *Procedure*

Take 100 ml of the solution, add sufficient concentrated sulphuric acid to make the strength of the solution 2 N with respect to sulphuric acid. Add 15 ml of ammonium thiocyanate solution and shake thoroughly. Titrate with standard mercurous nitrate solution, shaking throughout. When the red colour changes to brown or orange, warm the solution to 60 °C and complete the titration by adding drops of the reagent slowly until the colour just disappears.

8.4.5.1.2 *Calculation*

Calculate on the basis that 1 ml of decinormal mercurous nitrate solution is equivalent to 0.007 984 g of ferric oxide (Fe₂O₃).

8.4.5.2 *Determination of Titanium Dioxide*

8.4.5.2.1 *Procedure*

Take 2 ml of the standard titania solution in a 50 ml measuring flask and add 5 ml of hydrogen peroxide solution and 1 ml of phosphoric acid. Make up the volume to 50 ml and use as standard solution. Take about 20 ml of distilled water in another 50 ml measuring flask, add 5 ml of hydrogen peroxide solution and 1 ml of phosphoric acid. Then add the mixed oxide solution slowly [*see 8.4.4.4*] from a burette till the colour of the test solution is nearly of same intensity as that of

the standard. Make up the volume to 50 ml. Compare the intensities of the two solutions in an EEL Colorimeter using blue filter.

8.4.5.2.2 Calculation

$$\text{Titania (TiO}_2\text{) content, percent by mass} = \frac{x \times N \times 10^5}{y \times V}$$

where

x = reading of colorimeter with test solution,

N = mass, in g of titania per ml, of standard solution,

V = volume, in ml, of test solution required, and

y = reading of colorimeter with standard solution.

8.4.5.3 Determination of Phosphorus (as P₂O₅)

Determine phosphoric anhydride on a separate portion of ash (as prescribed under **7.15**).

8.4.6 Determination of Aluminium Oxide

8.4.6.1 Take 100 ml out of 250 ml portion of the mixed oxide solution [*see* **8.4.4.4**] and precipitate the mixed oxides in the usual manner (*see* **8.4.4**). Wash the precipitate with hot ammonium nitrate solution until free from sulphate. Remove the precipitate together with the filter paper preferably to a platinum crucible or porcelain crucible heated to constant mass. Char the filter paper slowly so that it does not burst into flame and ignite at 1 100 °C for about 2 h. Cool and weigh without delay. Repeat ignition to constant mass.

8.4.6.2 Deduct the mass of ferric oxide, titania and phosphorus pentoxide as determined under **8.4.5** from the total mass of the mixed oxide as determined under **8.4.6.1**. The difference represents the mass of alumina. Calculate as percentage on the mass of the material taken.

8.4.7 Determination of Calcium Oxide

8.4.7.1 To the filtrate from the separation of iron group [*see* **8.4.4.3**] add 1 ml of dilute hydrochloric acid, evaporate down to 200 ml and add 20 ml of boiling, ammonium oxalate solution to the boiling liquid. Add dilute ammonium hydroxide solution, drop by drop until the solution becomes just alkaline. Boil for 5 min and allow the precipitate of calcium oxalate to stand for 1 h at 90° C.

8.4.7.2 Filter the precipitate through a rapid low-ash filter paper (Whatman No. 40), and wash with hot water until free from chloride and oxalate. Dissolve the precipitate in 20 ml of dilute sulphuric acid and add 75 ml of hot water. Warm the solution to a temperature of 70 °C, and titrate with a decinormal solution of potassium permanganate.

8.4.7.3 Calculate on the basis that 1 ml of decinormal potassium permanganate is equivalent to 0.002 804 g of calcium oxide (CaO).

8.4.8 *Determination of Magnesium Oxide*

8.4.8.1 Evaporate the filtrate from calcium separation [see 8.4.7.2] a small volume until crystals separates. Cool, add 10 ml of concentrated nitric acid and slowly heat to hasten the decomposition of the ammonium salts. Repeat the operation with further 10 ml of concentrated nitric acid. Evaporate to dryness to remove nitric acid and cool. Add 20 ml of hot water to the dried mass followed by 2 ml of dilute hydrochloric acid, filter if any suspended impurities are found and dilute to 150 ml with water. Add 20 ml of diammonium hydrogen phosphate solution followed by 20 ml of concentrated ammonium hydroxide solution. Keep overnight in a cold place.

8.4.8.2 Filter through a rapid, low-ash filter paper (Whatman No. 40) and wash the precipitate with dilute ammonium hydroxide solution until the filtrate is free from chloride and phosphate. Transfer the precipitate with the filter paper into a porcelain crucible, char at a low heat so that the filter paper does not burst into flame. Raise the temperature to burn off carbon. Ignite the precipitate at a temperature of 1 100 °C for 1 h taking care to note that no black mass results. Cool and weigh.

8.4.8.3 Calculate on the basis that 1 g of magnesium pyrophosphate corresponds to 0.362 1 g of magnesium oxide (MgO).

8.4.9 *Determination of Oxide of Manganese*

Determine manganese as oxide of manganese (Mn₃O₄) as described under 7.14.

8.4.10 *Determination of Alkalis*

8.4.10.1 Spread a thin layer of calcium carbonate at the bottom of a Lawrence Smith crucible. Weigh about 0.8 g of finely ground bulk ash and mix with 0.8 g of ammonium chloride and 6.4 g of precipitated calcium carbonate by grinding together in an agate mortar. Carefully transfer the whole of the ground mixture to the Lawrence Smith crucible. Rinse the agate mortar with some more calcium carbonate and transfer into the crucible. Cover the mixture with a thin layer of calcium carbonate. Place the crucible through a hole in an asbestos pad, so that one-third of the crucible projects below the pad. Heat the crucible slowly with a small flame until odour of ammonia is no longer perceptible. In case, ammonium chloride sublimes out, slow down the rate of heating. Then heat the crucible for about 45 min in such a way that the lower portion of the crucible is at a dull-red heat.

8.4.10.2 Allow to cool, rinse the lid, and add 15 ml of hot water and digest in a steam bath for 10 min. Transfer the contents into a large agate mortar and crush the lumps. Transfer again into a porcelain basin or preferably a platinum basin. Wash the agate mortar several times to remove any residual particles, and sufficient water to the basin and digest for about half an hour. Filter through a rapid, low-ash filter paper (Whatman No. 40) into a beaker.

8.4.10.3 Wash the residue several times with hot water. Take the residue in the basin again and digest for half an hour and filter. Repeat this operation 3 to 4 times depending on the alkali content. Combine the filtrates. Add sufficient quantity of ammonium carbonate solution followed by dilute

ammonium hydroxide solution to precipitate the calcium. After the precipitate has settled filter. Wash the precipitate 4 or 5 times with hot water and dissolve in minimum quantity of dilute hydrochloric acid, and precipitate calcium as before. Filter again and combine the filtrates.

8.4.10.4 Evaporate the combined filtrate to dryness in porcelain basin and then decompose the ammonium salts in a muffle furnace maintained at 450 °C. Add hot water to the residue which will be dark in colour. Add 2 ml of dilute barium chloride solution to precipitate any sulphate. Then add a few millilitres of ammonium oxalate solution and 2 to 3 drops of concentrated ammonium hydroxide solution. Stand for 6 h or preferably overnight. Filter through a rapid, low-ash filter paper (Whatman No. 40) into a tared platinum basin and wash the residue with hot water. Evaporate the filtrate and washings to dryness and remove ammonium salts as before. Remove the dark stain by careful heating. Dissolve the residue in hot water, add 1 ml of dilute hydrochloric acid and evaporate to dryness. Then dry, heat the platinum basin in a muffle furnace maintained at 500 °C for half an hour. Cool and weigh. The difference in mass gives the mass of total alkali chlorides, that is mixed chlorides.

8.4.10.5 Carry out a blank determination with appropriate quantities of all the reagents but without the sample.

8.4.10.6 *Determination of sodium as sodium zinc uranyl acetate*

Dissolve the mixed chlorides in a small volume of water (2 ml). Treat the solution with 15 ml of zinc uranyl acetate reagent and stir vigorously for half an hour. Allow to stand for an hour and filter through a weighed sintered glass Gooch crucible No. 3. Wash the precipitate 3 times with 2 ml portions of the reagent and then four times with 2 ml portions of rectified spirit saturated with sodium zinc uranyl acetate and finally with ether. Dry at 105 °C for half an hour. Weigh as $\text{NaZn}(\text{UO}_2)_3 (\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$.

8.4.10.7 *Calculation*

$$\text{Mass of Na}_2\text{O} = 0.0202 \times \text{mass of NaZn}(\text{UO}_2)_3 (\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$$

$$\text{Mass of NaCl} = 0.0381 \times \text{mass of NaZn}(\text{UO}_2)_3 (\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$$

$$\text{Mass of KCl} = (\text{Total chlorides} - \text{amount of NaCl})$$

$$\text{Mass of K}_2\text{O} = \text{mass of KCl} \times 0.6314$$

8.5 Report

The results of analysis may be expressed as under:

<i>Sl No.</i>	<i>Constituents</i>	<i>Percent by mass</i>
(i)	Alumina (Al_2O_3)	
(ii)	Barium oxide (BaO)	
(iii)	Iron oxide (Fe_2O_3)	
(iv)	Lime (CaO)	
(v)	Magnesia (MgO)	

(vi)	Manganese oxide (Mn_3O_4)	
(vii)	Phosphorus pentoxide (P_2O_5)	
(viii)	Potassium oxide (K_2O)	
(ix)	Silica (SiO_2)	
(x)	Sodium oxide (Na_2O)	
(xi)	Sulphur trioxide (SO_3)	
(xii)	Titania (TiO_2)	