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Methods for

The analysis and testing of coal and coke —

Part 14: Analysis of coal ash and coke ash

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Co-operating organizations

The Solid Fuel Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

Association of Boiler Setters, Chimney and Furnace Constructors
Association of British Chemical Manufacturers*
Association of Consulting Engineers Incorporated
British Cast Iron Research Association
British Chemical Plant Manufacturers' Association
British Coal Utilisation Research Association*
British Coke Research Association*
British Coking Industry Association*
British Electrical and Allied Manufacturers' Association
British Iron and Steel Federation*
British Ironfounders' Association
British Mechanical Engineering Federation
Chamber of Coal Traders
Coal Utilisation Council
Coke Oven Managers' Association*
Combustion Engineering Association*
Council of Ironfoundry Associations
Electricity Council, the Generating Board and Area Boards in England and Wales*
Federation of British Industries*
Gas Council*
Heating and Ventilating Contractors Association
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National Coal Board*
Society of British Gas Industries
Water-tube Boilermakers' Association
Women's Advisory Council on Solid Fuel

The Government department and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

British Ceramic Research Association
British Coal Exporters' Federation
Cement Makers' Federation
D.S.I.R. — Warren Spring Laboratory
Institution of Electrical Engineers
London Coal Exporters' Association
London Transport Board
Society of Chemical Industry
Solid Smokeless Fuels Federation
South Wales Institute of Engineers

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Contents

Foreword

This standard makes reference to the following British Standards:

BS 410, *Test sieves*.

BS 1016, *Methods for the analysis and testing of coal and coke — Part 3: Proximate analysis of coal — Part 4: Proximate analysis of coke*.

BS 1017, *The sampling of coal and coke*.

BS 1041, *Code for temperature measurement*.

In 1942, when BS 1016, "*Methods for the analysis and testing of coal and coke*", was published it superseded a number of other standards, each dealing with special methods, bringing them up to date and embodying them in one standard. BS 1016:1942 also dealt with the receipt of samples and their preparation in the laboratory for analysis and was linked directly with a companion standard on methods of collection of samples, BS 1017, "*The sampling of coal and coke*".

Continued work by the Committee concerned and international discussion under the aegis of the International Organization for Standardization have led to the revision of these collected methods and a new edition of BS 1016 has become necessary. A similar revision of BS 1017 has been undertaken and the link between the two standards is maintained. The division between them, however, has been changed and this standard deals only with the analysis and testing of coal and coke; all the preparation of samples for analysis is included in the revised BS 1017.

The new standard is published in separate parts, each covering a particular group of analyses, e.g. proximate analysis, ultimate analysis. This method of presentation permits the revision of any part with the minimum of delay without the necessity of issuing a new comprehensive standard. Where the methods for a particular group of analyses for coke differ widely from those for coal they are published as a separate part but where the modifications for coke are slight they are given as separate sections of the same part.

In the interests of international discussion it is important that there should be uniformity in definition and in method of reporting of results. Each part of the new standard begins, therefore, with a list of definitions relevant to the methods described in it and ends with a section dealing with reporting of the results.

Part 14 — Analysis of coal ash and coke ash — deals with the determination of the major constituents common to all ashes. In March, 1960, BSI Document PD 3714 gave a brief review of the considerable progress which has been made in the development of more rapid techniques. The committee responsible for this revision of BS 1016 has now recommended the adoption of the B.C.U.R.A. rapid method1) which, as well as being accurate, enables several ashes to be analysed in the time taken for one by the classical method. The saving of time has been made by eliminating lengthy chemical separations and substituting selective complexometric and physico-chemical methods which utilize the relatively inexpensive spectrophotometers and flame photometers now available commercially.

A growing need for even more rapid methods of ash analysis has led to the development of a spectrochemical method, based on the use of the Hilger large quartz spectrograph, for the determination of some of the major constituents. Its precision is lower than that of the B.C.U.R.A. rapid method and so far, because of the high initial cost of the equipment, its use has been limited to a few laboratories. However, the possibility of future developments requiring large numbers of ash analyses warrants a description of the method in an Appendix.

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1) K. Archer, D. Flint and J. Jordan, Fuel, Lond., 1958, **37**, 421.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 18, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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14.1 Definitions

For the purposes of this British Standard, the following definitions apply:

14.1.1
ash (coal[2] and coke[3])

the inorganic matter remaining after the coal or coke has been incinerated to constant weight under standard conditions

14.1.2
within-laboratory tolerance

the maximum acceptable difference between determinations made in the same laboratory on the same preparation of ash by the same operator using the same apparatus

14.1.3
between-laboratory tolerance

the maximum acceptable difference between the means of two determinations carried out by two different laboratories on representative samples taken from the same preparation of ash

14.1.4
temperature measurement

where the temperature is specified as a definite figure, it is to be understood that this figure should be attained as closely as possible and that it should be subject only to the errors inherent in accurate temperature measurement, as defined in BS 1041[4]

where a range of temperature is given, the temperature may be anywhere in the range without detriment to the result. However, the mean of the range should be aimed at in order that errors of measurement do not cause a temperature outside the specified range to be used inadvertently

Table 1 — Characteristic composition of British coal and coke ashes

Constituent	Expressed as	Range per cent
Silica	SiO_2	15–55
Alumina	Al_2O_3	10–40
Ferric oxide	Fe_2O_3	1–40
Calcium oxide	CaO	1–25
Magnesium oxide	MgO	0.5–5
Sodium oxide	Na_2O	0–8
Potassium oxide	K_2O	0–5
Titanium oxide	TiO_2	0–3
Manganese oxide	Mn_3O_4	0–1
Sulphate	SO_3	0–12
Phosphate	P_2O_5	0–3

14.2 Introduction

One of the important factors governing the industrial usage of coal and coke is the behaviour of the mineral matter associated with it. The plant may be designed for this to be removed as particulate ash, fly ash, clinker or liquid slag and operational difficulties may be encountered if any other than the intended form of residue is produced. The analysis of ash prepared under standard condition[5] [6] is often used as a guide to the selection of suitable solid, fuel.

Ash consists mainly of the oxides of silicon, aluminium, iron, calcium, magnesium, titanium, manganese and the alkali metals, partly combined as silicates, sulphates and phosphates; its composition reflects the constitution of the original mineral matter. These constituents normally account for at least 99 per cent of the ash. The usual limits within which they are encountered are shown in Table 1, although the compositions of some ashes can be considerably outside these limits.

On exposure to air, some ashes rapidly absorb water and carbon dioxide. It is, therefore, necessary either to re-ignite each portion of ash immediately before weighing or to determine the loss on ignition using a separate portion. The results are reported on the "Ignited at 800 °C" basis.

Although the procedure is written for a single analysis of one ash, full advantage of the saving of time afforded by the method can best be taken by conducting several analyses simultaneously. The use of calibration graphs for these colorimetric methods leads to results which are less reproducible than those obtained by the specified procedure and is therefore not recommended.

14.3 Principle

The scheme of analysis is shown diagrammatically in Figure 1. Two solutions are prepared from the ash. Solution A is prepared by fusing the ash with sodium hydroxide, leaching the melt with water and acidifying with hydrochloric acid. It is used for the colorimetric determination of silica and alumina.

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[2] BS 1016-3, "*Proximate analysis of coal*".

[3] BS 1016-4, "*Proximate analysis of coke*".

[4] BS 1041, "*Code for temperature measurement*".

[5] BS 1016-3, "*Proximate analysis of coal*".

[6] BS 1016-4, "*Proximate analysis of coke*".

Solution B is prepared by decomposition of the ash with hydrofluoric, nitric and sulphuric acids. After removal of the silica by evaporation, the residue is dissolved in water. This solution is used for the flame photometric determination of sodium and potassium, the colorimetric determination of iron, titanium, manganese and phosphorus, and the determination of calcium and magnesium by titration with EDTA.

Separate portions of the sample are used for the gravimetric determination of sulphate and the determination of loss on ignition at 800 °C.

The spectrophotometer or flame photometer is calibrated for every determination using standard solutions prepared from salts of adequate purity or, in the case of silica and alumina, from either N.B.S. standard feldspar No. 99 or B.C.S. firebrick No. 269.

Unless otherwise stated, the coloured solutions prepared for optical density measurements are stable for several hours.

Should an abnormally low total be obtained, the oxides of other elements, e.g. arsenic, boron, barium, germanium and tin, may be present and, if desired, may be identified and determined by appropriate chemical or spectrographic methods. Substantial percentages of such oxides may influence the results of other analytical determinations.

14.4 Special apparatus

Muffle furnace. A muffle furnace[7] capable of giving a zone within the range 490–510 °C in 30 minutes from cold, of being raised to 790–810 °C in a further 60 to 90 minutes and of maintaining this latter temperature at the end of the run-up period. The ventilation shall be such as to give at least four air changes per minute at 800 °C[8].

Silica trays, 15 cm × 8 cm × 1 cm.

Silica plate, a silica plate 6 mm thick, which is an easy sliding fit into the muffle furnace.

Platinum crucibles, each of capacity 30 ml, with lid.

Cooling block, of aluminium.

Nickel crucibles, each of capacity 40 ml, with lid.

Spectrophotometer, of adequate sensitivity and selectivity[9].

Flame photometer, of adequate sensitivity and selectivity[10].

14.5 Coal or coke sample

The coal or coke used for the preparation of the sample of ash shall be prepared in a similar manner to the ½ lb analysis sample of coal or the 2 oz analysis sample of coke, taken according to BS 1017[11], ground to pass a 72 mesh BS test sieve[12] and thoroughly mixed, preferably by mechanical means. The weight of coal or coke necessary will vary with its ash content, but sufficient is required to provide at least 5 g of ash.

14.6 Preparation of ash

Using the silica trays, prepare 5 g of ash in the manner described for the determination of ash in coal (Part 3[13]) or coke (Part 4[14]). The loading of the trays shall not exceed 0.14 g/cm² for coal or 0.07 g/cm² for coke.

Grind the ash in an agate mortar so that it all passes a 240 mesh BS test sieve. Re-ignite the ash at 800 °C for one hour in the muffle furnace. Allow to cool, store in an airtight glass bottle of 1 oz capacity and mix thoroughly.

14.7 Loss on ignition

PRINCIPLE

One of two procedures may be adopted to minimize errors due to the absorption of water and carbon dioxide by the ash. Either the sample may be ignited at 800 °C to constant weight and cooled rapidly immediately before the portions for the preparation of the solutions are weighed out or the loss on ignition may be determined by the following procedure, using a separate portion of the sample weighed out at the same time as those for the rest of the analyses.

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[7] The high temperature muffle furnace described by C. W. G. Ockelford (Fuel, 1945, 24, 151) is suitable.

[8] The air changes per minute can be obtained by measurement of the air flow in the flue by means of a pitot-static tube and sensitive manometer [E. Owen, Measurement of Air-flow, 3rd Ed. Revised, p. 88 (Chapman & Hall, Lond.)].

[9] A Unicam S.P.600 or similar instrument is suitable.

[10] An "Eel" flame photometer or similar instrument is suitable.

[11] BS 1017, "*The sampling of coal and coke*".

[12] BS 410, "*Test sieves*".

[13] BS 1016-3, "*Proximate analysis of coal*".

[14] BS 1016-4, "*Proximate analysis of coke*".

PROCEDURE

Ignite a platinum crucible and lid[15], cool them on the cooling block and weigh to the nearest 0.1 mg. Introduce 0.45–0.55 g of ash. Weigh the covered crucible and its contents to determine the weight of ash taken. Place the uncovered crucible and the lid in the muffle furnace and ignite at 800 °C to constant weight. Cover the crucible with its lid and remove it from the furnace. Place the covered crucible on the cooling block and weigh when cool.

CALCULATION OF RESULT

W_1 = weight of crucible plus lid (g).

W_2 = weight of crucible plus lid plus ash before ignition (g).

W_3 = weight of crucible plus lid plus ash after ignition (g).

L = percentage loss on ignition at 800 °C.

$$L = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

14.8 Preparation of solutions

In the preparation of solutions and in the subsequent analyses, all reagents obtainable in analytical reagent quality shall be used as such; others shall be of the purest grade available. Distilled water shall be used throughout.

14.8.1 Solution A

SPECIAL REAGENTS

Sodium hydroxide, pellets.

Hydrochloric acid, d = 1.18.

Reference standard, soda feldspar (N.B.S. Sample No. 99) or firebrick (B.C.S. Sample No. 269). Dry for 1 hour at 105 °C before use.

PROCEDURE

Weigh accurately[16] about 50 mg of ash, transfer it to a nickel crucible and add 1.5 g of the sodium hydroxide: Cover the crucible and heat gently over a micro bunsen burner until the sodium hydroxide is molten. If the ash floats on the molten sodium hydroxide, swirl the contents of the crucible until the ash sinks[17]. Finally heat for 5 minutes at a dull red heat. Allow the crucible to cool, half fill it with water, cover and allow to stand for two hours. Transfer the contents of the crucible, through a long stemmed polythene[18] funnel, to a one-litre graduated flask containing about 400 ml of water and 10 ml of the hydrochloric acid. Using a rubber "policeman", remove any residue from the crucible and wash it into the flask. Dilute to 1 litre and mix well. Allow the solution to stand until any slight turbidity has disappeared[19].

Prepare two reference standard solutions[20] exactly as described above, but using about 35 mg of the reference standard for each, instead of about 50 mg of ash. Also prepare an overall blank solution in exactly the same way but omitting the sample.

14.8.2 Solution B

SPECIAL REAGENTS

Hydrofluoric acid, 40 per cent, w/w.

Sulphuric acid, dilute (1 + 1).

Nitric acid, d = 1.42.

PROCEDURE

Weigh accurately about 0.4 g of ash into a platinum crucible. Add 1.5 ml of the sulphuric acid and about 10 ml of the hydrofluoric acid. Place the lid on the crucible and digest on a water bath for 1 hour. Remove and rinse the lid, collecting the washings in the crucible, and allow the solution to evaporate on the water bath until most of the hydrofluoric acid and water have been removed. Transfer the crucible to a hot-air bath, evaporate to dense white fumes of sulphuric acid and fume for 10 minutes. Allow to cool, add 1 ml of the sulphuric acid and 1 ml of the nitric acid. Evaporate to fumes of sulphuric acid, heat for a further 10 minutes and allow to cool.

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[15] It is sufficient to ignite the empty crucible and lid to bright redness for ten minutes, using a Méker or similar burner.

[16] It is preferable to use a balance capable of weighing to 0.01 mg.

[17] If this is ineffective, allow the melt to solidify momentarily, so that the floating ash is drawn below the surface, and then continue heating gently.

[18] The terms "polythene" and "polyethylene" are synonymous.

[19] The turbidity, due to iron and manganese hydroxides, disappears on standing, usually in about one hour; the solution may conveniently be left overnight.

[20] It is only necessary to prepare reference standard solutions for each batch of samples; two are prepared to increase the accuracy of the determinations.

Add about 20 ml of water to the crucible and digest on a water bath for half an hour. Transfer the solution to a 400 ml beaker, dilute to about 250 ml and simmer until all soluble matter has dissolved. Allow to cool and filter if necessary[21]. Transfer the solution to a 500 ml graduated flask, dilute to 500 ml and mix thoroughly[22].

Prepare an overall blank solution exactly as described above but omitting the ash.

14.9 Silica

SPECIAL REAGENTS

Sulphuric acid, dilute (1 + 1).

Ammonium molybdate solution. Dissolve 7.5 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 75 ml of water. Add 10 ml of the sulphuric acid and dilute to 100 ml. Store in a polythene[23] bottle.

Tartaric acid solution, 10 per cent, w/v. Store in a polythene[23] bottle.

Reducing solution. Dissolve 0.7 g of sodium sulphite, $Na_2SO_3.7H_2O$, in 10 ml of water. Add 0.15 g of 1-amino-2-naphthol-4-sulphonic acid and stir until dissolved. Dissolve 9 g of sodium metabisulphite in 90 ml of water, add this solution to the solution of sodium sulphite and 1-amino-2-naphthol-4-sulphonic acid and mix thoroughly. Prepare freshly before use.

PROCEDURE

Pipette into separate 100 ml graduated flasks 10 ml of the ash solution A, 10 ml of each reference standard solution A and 10 ml of the overall blank solution A. Dilute each to about 50 ml and pipette 1 ml of the ammonium molybdate solution into each flask. Mix well and allow to stand for ten minutes. Into each flask in turn pipette 4 ml of the tartaric acid solution, followed immediately by 1 ml of the reducing solution, swirling the flask during the additions. Immediately dilute the contents of the flask to 100 ml and mix thoroughly before proceeding to the next flask.

Fill two 2 cm cells with water and, using the spectrophotometer, compare their optical densities at 650 nm. Select the less dense as the comparison cell and use the other for the contents of the flasks.

After a minimum time of 1 hour, measure the optical density of the contents of each flask against water.

CALCULATION OF RESULT

W_1 = weight of ash in solution A (mg).

W_2, W_3 = weight of reference standard in reference standard solutions A (mg).

D_1 = observed optical density from the ash solution.

D_2, D_3 = observed optical densities from the reference standard solutions.

D_4 = observed optical density from the overall blank solution.

d_1 = optical density equivalent to 50 mg of ash $\left[d_1 = \frac{50(D_1 - D_4)}{W_1}\right]$.

d_2, d_3 = optical densities equivalent to 50 mg of reference standard[a]

$$\left(d_2 = \frac{50(D_2 - D_4)}{W_2};\ d_3 = \frac{50(D_3 - D_4)}{W_3}\right).$$

S = percentage of silica in the reference standard.

SiO_2 = percentage of silica in the ash.

$$SiO_2 = \frac{2S\ d_1}{d_2 + d_3}$$

[a] If d_2 and d_3, differ by more than 0.010, the procedure shall be repeated.

14.10 Alumina

SPECIAL REAGENTS

Acetic acid, glacial.

Hydrochloric acid, dilute (1 + 1).

Calcium chloride solution. Dissolve 14 g of calcium carbonate in 50 ml of the hydrochloric acid. Boil the solution for 2 minutes. Cool and dilute to 1 litre.

Hydroxyammonium chloride solution, 10 per cent, w/v.

Thioglycollic acid solution, dilute (1 + 19). Prepare freshly before use.

Buffer solution. Dissolve 140 g of hydrated sodium acetate, $CH_3.COONa.3H_2O$, in water. Add 60 ml of the acetic acid and dilute to 1 litre.

Alizarin red-S solution, 0.1 per cent, w/v.

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[21] A small quantity of an insoluble residue, usually corundum or barium sulphate, may remain at this stage; it can be filtered off, weighed and identified, if desired.

[22] In order to minimize possible contamination from glass vessels, sodium and potassium should be determined immediately after the preparation of solution B.

[23] The terms "polythene" and "polyethylene" are synonymous.

Procedure

Pipette into separate 100 ml graduated flasks 5 ml of the ash solution A, 5 ml of each reference standard solution A and 5 ml of the overall blank solution A. Dilute each to about 50 ml. Add from pipettes, in the following order, mixing thoroughly after the addition of each reagent, 2 ml of the calcium chloride solution, 1 ml of the hydroxyammonium chloride solution, 1 ml of the thioglycollic acid solution and 10 ml of the buffer solution. Into each flask in turn pipette 5 ml of the alizarin red-S solution, dilute to 100 ml and mix thoroughly before proceeding to the next flask.

After three hours[24], fill two 2 cm cells with the overall blank solution[25] and, using the spectrophotometer, measure the difference between their optical densities at 475 nm. Select the less dense for the overall blank solution and the other for the sample and reference standard solutions. Measure the optical density of the sample solution and the reference standard solutions against the overall blank solution. Correct the observed optical density of each solution for the difference in optical density between the cells.

The iron present is not completely complexed by the thioglycollic acid and interferes slightly.
At 475 nm, 1 per cent of Fe_2O_3 produces an optical density equivalent to 0.01 per cent of Al_2O_3 and a correction for this is necessary.

Calculation of result

W_1 = weight of ash in solution A (mg).

W_2, W_3 = weight of reference standard in reference standard solution A (mg).

D_1 = optical density (corrected for the cell difference) from the ash solution.

D_2, D_3 = optical densities (corrected for the cell difference) from the reference standard solutions.

d_1 = optical density equivalent to 50 mg of ash $\left[d_1 = \dfrac{50D_1}{W_1}\right]$.

d_2, d_3 = optical densities equivalent to 50 mg of reference standard[a] $\left(d_2 = \dfrac{50D_2}{W_2};\ d_3 = \dfrac{50D_3}{W_3}\right)$.

A = percentage of alumina in the reference standard.

Fe_2O_3 = percentage of iron oxide in the sample of ash (see Clause **14.12**).

Al_2O_3 = percentage of alumina in the sample of ash

$$Al_2O_3 = \frac{2Ad_1}{d_2 + d_3} - 0.01Fe_2O_3.$$

[a] If d_2 and d_3 differ by more than 0.004 the procedure shall be repeated.

14.11 Sodium oxide and potassium oxide

Special reagents

Sulphuric acid, approximately 0.02N.

Concentrated sodium and potassium solution. Dissolve 0.1886 g of sodium chloride and 0.1583 g of potassium chloride (both dried at 400 °C for one hour) in the sulphuric acid and dilute to 1 litre with the acid. Store in a polythene[26] bottle.

Standard sodium and potassium solution. Dilute 100 ml of the concentrated standard solution to 1 litre with the sulphuric acid and store in a polythene[23] bottle. This solution contains 10 p.p.m. Na_2O and 10 p.p.m. K_2O.

Procedure

Pipette into separate 100 ml graduated flasks 25 ml of the ash solution B[27] and 25 ml of the overall blank solution B. Dilute to 100 ml and mix thoroughly.

With the sodium filter in position and using the sulphuric acid, set the flame photometer to indicate zero. Using the standard sodium and potassium solution, adjust the flame photometer to give the full scale deflection. Record the readings of the ash and overall blank solutions. Replace the sodium filter by the potassium filter and re-adjust the flame photometer to give zero and full scale deflections, in the same manner as for sodium. Record the readings of the ash and overall blank solutions.

Using the calibration graphs, read off the concentrations of sodium oxide and potassium oxide in the ash solution and in the overall blank solution.

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[24] The optical density is stable between 2½ and 4 hours from the time of adding the alizarin red-S solution.

[25] To obtain adequate sensitivity, the overall blank solution is used in the comparison cell, in preference to water, because it absorbs appreciably at 475 nm.

[26] The terms "polythene" and "polyethylene" are synonymous.

[27] This aliquot is suitable for an ash containing up to 5 per cent of sodium oxide or potassium oxide; if a full scale deflection is obtained, repeat the determination, taking smaller aliquots of both sample and overall blank solutions and calculating accordingly.

PREPARATION OF CALIBRATION GRAPHS

Add 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 ml of the concentrated sodium and potassium solution to a series of 100 ml graduated flasks. Dilute each solution to 100 ml with the sulphuric acid and mix thoroughly.

These solutions are equivalent to 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 p.p.m. respectively of both sodium oxide and potassium oxide.

Carry out the procedure described in the second paragraph above, i.e. "with the sodium filter . . . as for sodium", using the solutions equivalent to 0 and 10 p.p.m. of both sodium oxide and potassium oxide to set the instrument and recording the readings of all the other solutions.

Prepare calibration graphs, plotting the instrument readings against the concentration in p.p.m. separately for sodium oxide and potassium oxide. The graphs are not necessarily linear.

CALCULATION OF RESULTS

Sodium oxide

W = weight of ash in solution B (g).

C_1 = p.p.m. of sodium oxide from the ash solution.

C_2 = p.p.m. of sodium oxide from the overall blank solution.

Na_2O = percentage of sodium oxide in the ash (see Note).

$$Na_2O = \frac{C_1 - C_2}{5W}$$

Potassium oxide

W = weight of ash in solution B (g).

C_3 = p.p.m. of potassium oxide from the ash solution.

C_4 = p.p.m. of potassium oxide from the overall blank solution.

K_2O = percentage of potassium oxide in the ash.

$$K_2O = \frac{C_3 - C_4}{5W}$$

NOTE Calcium oxide causes a slight enhancement of the flame photometer reading for sodium but the presence of aluminium and sulphuric acid both minimize the effect; only in the case of exceptional ashes where the level of calcium oxide reaches 30 per cent does the error in the determination of sodium oxide exceed 0.1 per cent.

14.12 Iron oxide

SPECIAL REAGENTS

Acetic acid, glacial.

Sulphuric acid, dilute (1 + 1).

Hydrogen peroxide, 30 per cent, w/v (100 vol).

Tiron solution. Dissolve 3.25 g of Tiron (catechol 3 : 5 disulphonic acid, disodium salt) in water and dilute to 50 ml. Prepare immediately before use.

Buffer solution. Dissolve 135 g of ammonium acetate, $CH_3.COONH_4$, in water, add 50 ml of the acetic acid and dilute to 1 litre.

Standard iron solution. Transfer 0.5893 g of ammonium ferrous sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, to a 400 ml beaker. Add 100 ml of water, 6 ml of the sulphuric acid and a few drops of the hydrogen peroxide. Boil to remove the excess hydrogen peroxide. Cool and dilute to 1 litre in a graduated flask. 5 ml of this solution are equivalent to 0.6 mg of Fe_2O_3 (see Note).

PROCEDURE

Pipette into separate 50 ml graduated flasks 5 ml of the ash solution B, 5 ml of the overall blank solution B and 5 ml of the standard iron solution. Another flask is required for the reagent blank. Add about 20 ml of water to each flask. Pipette 2 ml of the Tiron solution and 15 ml of the buffer solution into each flask, dilute to 50 ml and mix thoroughly.

Fill two 1 cm cells with water and, using the spectrophotometer, compare their optical densities at 560 nm. Select the less dense as the comparison cell and use the other for the contents of the flasks. Measure the optical density of the contents of each of the flasks against water.

The optical densities can be measured immediately and the colour is stable for at least two hours. Reserve the remainder of each solution (with the exception of the standard iron solution) for the determination of titanium.

CALCULATION OF RESULT

W = weight of ash in solution B (g).

D_1 = observed optical density from the ash solution.

D_2 = observed optical density from the overall blank solution.

D_3 = observed optical density from the standard iron solution.

D_4 = observed optical density from the reagent blank solution.

Fe_2O_3 = percentage of iron oxide in the ash.

$$Fe_2O_3 = \frac{6(D_1 - D_2)}{W(D_3 - D_4)}$$

NOTE If there is any doubt concerning the purity of the ammonium ferrous sulphate used for the preparation of the standard iron solution, the total iron content (Fe) as mg Fe_2O_3/5 ml shall be accurately determined; the percentage of ferric oxide in the sample will then be given by:

$$Fe_2O_3 = \frac{10Fe(D_1 - D_2)}{W(D_3 - D_4)}$$

14.13 Titanium oxide

SPECIAL REAGENTS

Acetic acid, glacial.

Sulphuric acid, d = 1.84.

Sulphuric acid, dilute (1 + 39).

Tiron solution. Dissolve 3.25 g of Tiron (catechol 3 : 5 disulphonic acid, disodium salt) in water and dilute to 50 ml. Prepare immediately before use.

Buffer solution. Dissolve 135 g of ammonium acetate, $CH_3.COONH_4$, in water, add 50 ml of the acetic acid and dilute to 1 litre.

Sodium dithionite, $Na_2S_2O_4 + H_2O$. Minimum assay (iodometric) 85 per cent $Na_2S_2O_4$[28].

Concentrated titanium solution. Transfer 0.450 g of potassium titanium oxalate, $K_2TiO(C_2O_4)_2.2H_2O$, and 0.8 g of ammonium sulphate to a 100 ml Kjeldahl flask. Add 5 ml of the sulphuric acid (d = 1.84) and heat gradually. Boil for ten minutes. Cool and dilute to 100 ml.

Standard titanium solution. Dilute 10 ml of the concentrated titanium solution to 1 litre with the dilute sulphuric acid. 5 ml of this solution are equivalent to 0.05 mg TiO_2.

PROCEDURE

Pipette 5 ml of the standard titanium solution into a 50 ml graduated flask and add about 20 ml of water. Pipette 2 ml of the Tiron solution and 15 ml of the buffer solution into the flask, dilute to 50 ml and mix thoroughly.

Fill two 4 cm cells with water and, using the spectrophotometer, compare their optical densities at 430 nm. Select the less dense as the comparison cell and use the other for the contents of the flasks.

Treat the titanium standard and the solutions reserved from the iron determination (Clause **14.12**) consecutively as follows:

Add, to one flask only, 10–20 mg of sodium dithionite, shake gently to dissolve and measure the optical density of the solution against water as soon as the purple colour due to iron has disappeared. Repeat the procedure given in the last sentence on each flask in turn[29].

CALCULATION OF RESULT

W = weight of ash in solution B (g).

D_1 = observed optical density from the ash solution.

D_2 = observed optical density from the overall blank solution.

D_3 = observed optical density from the standard titanium solution.

D_4 = observed optical density from the reagent blank solution.

TiO_2 = percentage of titanium oxide in the ash.

$$TiO_2 = \frac{D_1 - D_2}{2W(D_3 - D_4)}$$

14.14 Manganese oxide

SPECIAL REAGENTS

Potassium periodate, KIO_4.

Sulphuric acid, d = 1.84.

Phosphoric acid, d = 1.75.

Concentrated manganese solution. Dissolve 1.036 g of potassium permanganate in about 500 ml of water. Reduce the solution with sulphur dioxide, boil off the excess gas, cool and dilute to 1 litre.

Standard manganese solution. Dilute 10 ml of the concentrated manganese solution to 1 litre. 50 ml of this solution are equivalent to 0.25 mg of Mn_3O_4.

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[28] Sodium dithionite may deteriorate on prolonged storage.

[29] The colour due to the ferric iron-Tiron complex reappears on standing.

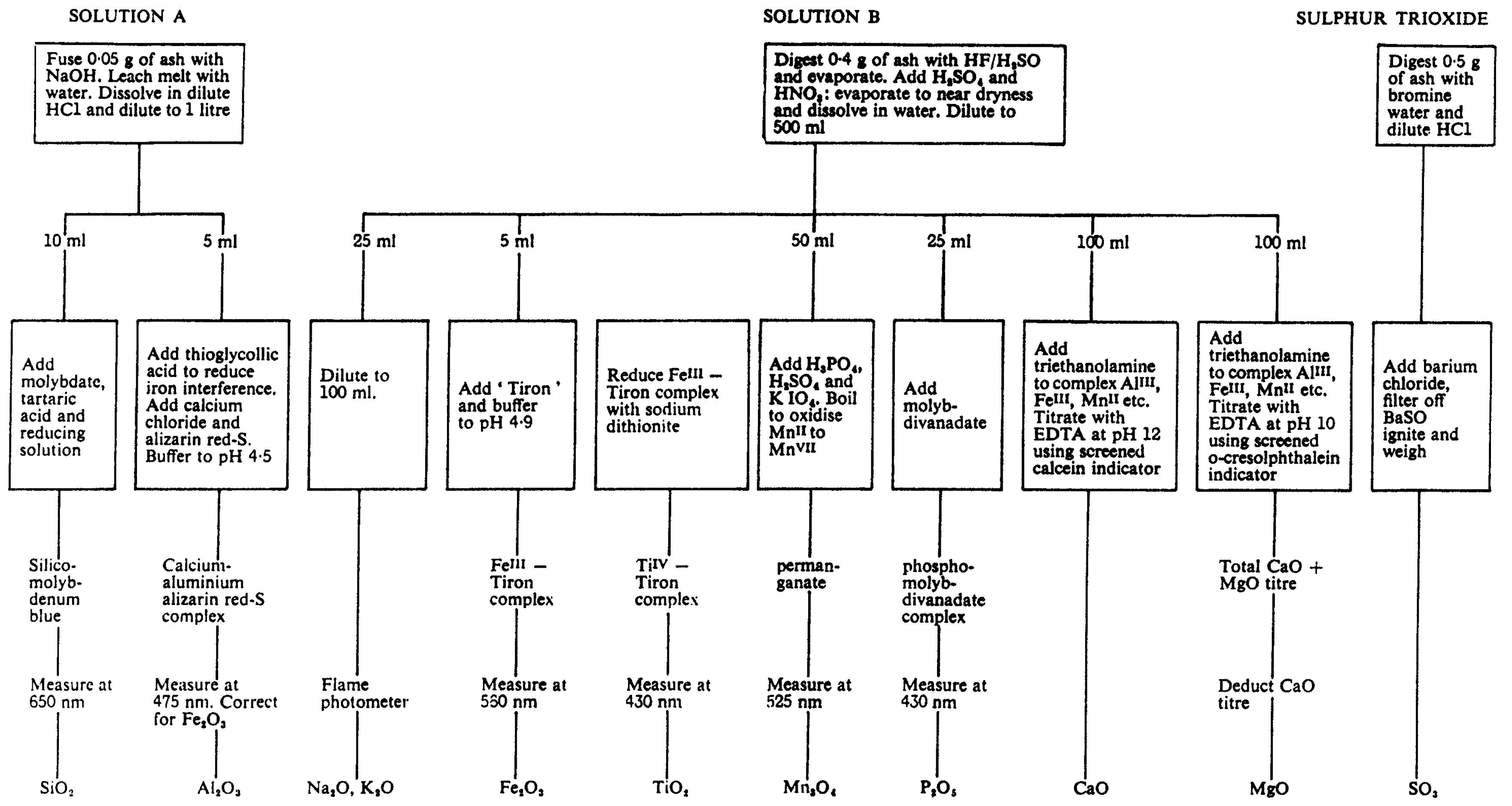

Figure 1 — Scheme of analysis of coal ash and coke ash

PROCEDURE

Pipette into separate 250 ml beakers 50 ml of the ash solution B, 50 ml of the overall blank solution B and 50 ml of the standard manganese solution. A further beaker containing about 50 ml of water is required for the reagent blank. Add to each of the beakers, 3 ml of the sulphuric acid, 1 ml of the phosphoric acid and 0.5 g of the potassium periodate. Cover the beakers and boil the contents for five minutes. Maintain the solutions just below boiling point for a further 30 minutes, allow to cool to room temperature, transfer to 100 ml graduated flasks, dilute to 100 ml and mix thoroughly.

Fill two 4 cm cells with water and, using the spectrophotometer, compare their optical densities at 525 nm. Select the less dense as the comparison cell and use the other for the contents of the flasks. Measure the optical densities of the contents of each of the flasks against water.

CALCULATION OF RESULT

W = weight of ash in solution B (g).

D_1 = observed optical density from the ash solution.

D_2 = observed optical density from the overall blank solution.

D_3 = observed optical density from the standard solution.

D_4 = observed optical density from the reagent blank solution.

Mn_3O_4 = percentage of manganese oxide in the ash.

$$Mn_3O_4 = \frac{D_1 - D_2}{4W(D_3 - D_4)}$$

14.15 Phosphorus pentoxide

SPECIAL REAGENTS

Nitric acid, dilute (1 + 1).

Molybdivanadate solution. Dissolve 1.25 g of ammonium metavanadate, NH_4VO_3, in 400 ml of the nitric acid. Dissolve 50 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 400 ml of water. Pour the ammonium molybdate solution into the metavanadate solution, while stirring. Dilute to 1 litre and mix.

Concentrated phosphorus solution. Dissolve 0.3835 g of potassium dihydrogen phosphate, KH_2PO_4, (dried for 1 hour at 110 °C before weighing) in water and dilute to 1 litre.

Standard phosphorus solution. Dilute 50 ml of the concentrated phosphorus solution to 1 litre. 25 ml of this solution are equivalent to 0.25 mg of P_2O_5.

PROCEDURE

Pipette into separate 50 ml graduated flasks 25 ml of the ash solution B, 25 ml of the overall blank solution B and 25 ml of the standard phosphorus solution. Another flask is required for the reagent blank. Pipette 10 ml of the molybdivanadate solution into each flask, swirling it during the addition. Dilute to 50 ml, mix thoroughly and allow to stand for at least five minutes.

Fill two 4 cm cells with water and, using the spectrophotometer, compare their optical densities at 430 nm. Select the less dense as the comparison cell and use the other for the contents of the flasks. Measure the optical densities of the contents of each of the flasks against water.

CALCULATION OF RESULT

W = weight of ash in solution B (g).

D_1 = observed optical density from the ash solution.

D_2 = observed optical density from the overall blank solution.

D_3 = observed optical density from the standard phosphorus solution.

D_4 = observed optical density from the reagent blank solution.

P_2O_5 = percentage of phosphorus pentoxide in the ash.

$$P_2O_5 = \frac{D_1 - D_2}{2W(D_3 - D_4)}$$

14.16 Calcium oxide and magnesium oxide

SPECIAL REAGENTS

Hydrochloric acid, d = 1.18.

Hydrochloric acid, dilute (1 + 24).

Triethanolamine solution. Dilute 500 ml of triethanolamine to 1 litre with water and mix thoroughly.

Ammonium hydroxide solution, d = 0.88.

Sodium hydroxide solution. Dissolve 160 g of sodium hydroxide in water and dilute to 1 litre. Store in a polythene[30)] bottle.

[30)] The terms “polythene” and “polyethylene” are synonymous.

Standard calcium solution (*containing magnesium*[31]). Dissolve 1.785 g of calcium carbonate, dried at 110 °C, in 100 ml of the dilute hydrochloric acid, boil to expel carbon dioxide and cool. Dissolve 1.2–1.25 g of magnesium sulphate, $MgSO_4.7H_2O$, in the solution and dilute to 1 litre. 1 ml of this solution is equivalent to 1 mg of CaO.

Calcein indicator. Mix together by grinding, in a suitable mortar, 0.2 g of calcein, 0.12 g of thymolphthalein and 20 g of potassium chloride.

o-cresolphthalein indicator. Dissolve 0.1 g of o-cresolphthalein-di (methyl-iminodiacetic acid), 0.005 g of methyl red and 0.05 g of paramine green BN in a few drops of the ammonium hydroxide solution and dilute to 100 ml. This solution should not be kept longer than one week and should preferably be prepared freshly each day.

EDTA solution. Dissolve 6.6 g of the disodium salt of diaminoethane-tetra-acetic acid (EDTA) in water and dilute to 1 litre. Pipette 25 ml of the standard calcium solution into each of four flasks. Add to each flask the reagents specified in the procedure for the determination of calcium oxide and titrate with the EDTA solution. Calculate the calcium oxide equivalent in milligrammes of 1 ml of the EDTA solution.

PROCEDURE

a) *Titration of calcium oxide*

Pipette into separate 500 ml conical flasks 100 ml of the ash solution B and 100 ml of the overall blank solution B. Pipette into each flask 5 ml of the standard calcium solution, add 20 drops of the hydrochloric acid ($d = 1.18$), 5 ml of the triethanolamine solution, 5 ml of the ammonium hydroxide solution and 10 ml of the sodium hydroxide solution, mixing thoroughly after the addition of each reagent[32]. Dilute each solution to about 200 ml with water. Add about 40 mg of the calcein indicator to each flask and titrate[33] with the EDTA solution until the colour changes from a fluorescent green to purple[34].

b) *Titration of calcium oxide plus magnesium oxide*

Pipette into separate 500 ml conical flasks 100 ml of the ash solution B and 100 ml of the overall blank solution B. Pipette into each flask 5 ml of the standard calcium solution, add 20 drops of the hydrochloric acid ($d = 1.18$), 20 ml of the triethanolamine solution and 25 ml of the ammonium hydroxide solution, mixing thoroughly after the addition of each reagent. Dilute each solution to about 200 ml with water. Add 0.5 ml of the o-cresolphthalein indicator to each flask and titrate with the EDTA solution until the colour changes from pale purple to colourless or very pale grey[35].

CALCULATION OF RESULTS

W = weight of ash in solution B (g).

V_1 = volume of EDTA used in the titration of the ash solution in the determination of calcium oxide.

V_2 = volume of EDTA used in the titration of the overall blank solution in the determination of calcium oxide.

V_3 = volume of EDTA used in the titration of the ash solution in the determination of calcium oxide plus magnesium oxide.

V_4 = volume of EDTA used in the titration of the overall blank solution in the determination of calcium oxide plus magnesium oxide.

F = weight of calcium oxide (mg) equivalent to 1 ml of EDTA.

CaO = percentage of calcium oxide in the ash.

MgO = percentage of magnesium oxide in the ash.

$$CaO = \frac{F(V_1 - V_2)}{2W}$$

$$MgO = \frac{0.3595F}{W}(V_3 - V_4 - V_1 + V_2).$$

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[31] Magnesium is incorporated in this solution so that a single solution suffices both for the standardization of the EDTA and for the determinations; the exact amount of magnesium sulphate is not critical but it is important to use the same batch of standard solution for both the ash and the blank solutions.

[32] Occasionally samples may be found to contain a relatively high (> 2 : 3) magnesium to calcium ratio. It has been shown by R. D. Bond and B. M. Tucker (Chem. and Ind., 1954, 1236) that calcium may be coprecipitated with or adsorbed onto the magnesium hydroxide precipitate. In these cases, the addition of 1 ml of a 20 per cent sucrose solution before the addition of the other reagents was found to reduce the error considerably.

[33] If the phosphorus content of the sample is high, the titration should be carried out slowly.

[34] At the end point the purple colour is not intensified by the addition of more EDTA solution; the end point of this titration is most easily observed in diffuse daylight or in the light given by "colour matching" fluorescent tubes (6 500 °K).

[35] An excess of EDTA produces a green colouration at this stage.

14.17 Determination of sulphur trioxide

SPECIAL REAGENTS

Bromine water, saturated.

Hydrochloric acid, d = 1.18.

Hydrochloric acid, dilute (1 + 9).

Barium chloride solution, 10 per cent, w/v.

Potassium sulphate solution. Dissolve about 2 g of potassium sulphate in water and dilute to 1 litre.

Methyl red indicator. Dissolve 0.02 g of methyl red in 60 ml of ethanol (95 per cent) or industrial spirit; dilute to 100 ml with water.

PROCEDURE

Weigh accurately about 0.5 g of the ash and transfer to a 250 ml beaker. A further beaker is required for the blank determination. Add to each beaker 5 ml of the bromine water and 100 ml of the dilute hydrochloric acid. Cover the beakers and boil for one hour. Filter each solution through an ashless, close textured, double acid washed paper[36) into a 400 ml beaker, washing the paper with four 20 ml portions of hot water. Neutralize the filtrates with the ammonium hydroxide solution, using the methyl red indicator, and then add 1 ml of the hydrochloric acid ($d = 1.18$).

Dilute each solution to about 200 ml with water and from a pipette add 25 ml of the potassium sulphate solution. Boil the solutions, add 10 ml of the barium chloride solution from a pipette, held so that the liquid falls into the middle of the boiling solution, and maintain just below the boiling point for 30 minutes. Transfer each precipitate on to an ashless, close textured, double acid washed paper[36) and wash with water until free from chloride. Fold the wet filter papers and place them in silica crucibles which have been previously ignited and weighed. Stand the crucibles on the silica plate and place them in the muffle furnace at 800 °C. Ignite for 15 minutes, remove the crucibles, place in a desiccator to cool and weigh.

CALCULATION OF RESULT

W_1 = weight of ash taken (g).

W_2 = weight of barium sulphate from ash solution (g).

W_3 = weight of barium sulphate from blank solution (g).

SO_3 = percentage of sulphur trioxide in the ash.

$$SO_3 = \frac{34.3(W_2 - W_3).}{W_1}$$

14.18 Tolerances

The figures below are actual differences in per cent between duplicates.

	Within-laboratory tolerance	**Between-laboratory tolerance**
Silica	0.6	2.0
Alumina	0.6	2.0
Iron oxide	0.3	0.5
Calcium oxide	0.2	0.5
Magnesium oxide	0.2	0.5
Sodium oxide	0.1	0.2
Potassium oxide	0.1	0.5
Titanium oxide	0.05	0.1
Manganese oxide	0.05	0.05
Sulphur trioxide	0.2	0.2
Phosphorus pentoxide[a]	0.05	0.15

[a] Although the within-laboratory tolerance quoted here is in line with that given in BS 1016-9, "*Phosphorus in coal and coke*", this is not so for the between-laboratory tolerance; this matter is under investigation.

These figures apply to most British coal ashes, but may be exceeded for any constituent present in abnormal concentration. For some constituents, in particular for the oxides of phosphorus, potassium and sodium, there is evidence to suggest that the between-laboratory tolerance depends directly on concentration.

14.19 Reporting of results

If necessary, calculate the results to an "Ignited at 800 °C" basis as follows:

L = percentage loss on ignition at 800 °C.

Multiply the percentages of the constituents by

$$\frac{100}{100 - L}$$

[36) A Whatman No. 42 is suitable.

Appendix Spectrochemical analysis

A.1 Introduction

Spectrochemical methods of ash analysis are useful where an even higher rate of output than that obtainable by the B.C.U.R.A. method is desired and the accuracy requirements are less stringent. It is possible for two operators, determining silicon, aluminium, iron, calcium, magnesium, titanium and manganese, to average some two dozen analyses per day[37]. If the remaining elements are required, the methods specified for their determination in the foregoing section may be used.

A.2 Principle

The ash is dissolved by fusion with a borate-carbonate mixture. The glass so formed is dissolved in dilute nitric acid containing a known amount of chromium (Note 1). The resulting solution is introduced into an uncontrolled condensed spark (Note 2) using either a vacuum cup or a rotating disk graphite electrode. The light emitted is separated into its component wavelengths by refraction and dispersion in the optical system of the spectrograph and is recorded on a photographic plate as a series of images of the spectrograph slit. The wavelength of each line is characteristic of one or other of the elements excited by the spark and its density is a function of the amount of that element present. Thus, by comparing the density of suitable pairs of lines, one being characteristic of an element in the sample and the other of chromium, a known amount of which is present, a quantitative analysis of the sample can be obtained. Errors due to variations in the characteristics of the emulsion are minimized by calibrating every plate.

A.3 Special apparatus

Platinum crucible, capacity 35 ml, with lid.

Spectrograph[38], covering the range 2 550–3 850 Å in one exposure and capable of completely resolving the Si I 2881.6Å and the Cr I 2881.9Å lines when used with a slit width of 0.02 mm.

Spark source. A suitable arrangement for producing an uncontrolled condensed spark discharge, consists of a 0.25 kW transformer having a minimum potential on open circuit of 15 kV r.m.s. (wound so as to have a low leakage inductance) and a capacitance of 0.005 μF in parallel across the secondary. The nominal inductance of the discharge circuit must be reduced to a minimum, e.g. by using straight, well spaced leads.

D.C. source, capable of supplying 300 V at 5A.

Rotating sector, seven-step, having a 2 : 1 exposure ratio between steps and rotating at about 400 rev/min. The speed is chosen so as to avoid stroboscopic effects.

Electrode systems.

1. Vacuum cup. The design described by Zink[39] is suitable.
2. Rotating disk. The design described by Philcox[40] is suitable.
3. Iron-carbon arc, between iron and carbon rods of diameter ⅛–¼ inch.
4. In the above electrode systems the graphite counter-electrode should be a truncated cone having an included angle of 40° and a 2 mm flat.

Densitometer, non-recording, capable of measuring line densities up to a value of two.

A.4 Special reagents

Fusion mixture. Thoroughly mix five parts of pure anhydrous sodium carbonate with three parts of pure prefused borax ground to pass a 36 mesh BS sieve.

Nitric acid, dilute (1 + 4).

Nitric acid, dilute (12 + 88).

Nitric acid, dilute (7 + 93).

Reference standard solution. Dissolve 6.000 g potassium dichromate (dried at 150 °C for 1 hour) in the nitric acid (12 + 88) to make 1 litre of solution.

Hydrogen peroxide, 30 per cent, w/v (100 vol).

A.5 Photographic equipment

Photographic plates. Unbacked slow fine-grain high contrast plates[41].

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[37] K. Dixon, Analyst, 1958, **83**, 382.

[38] The Hilger large quartz spectrograph is suitable.

[39] T. H. Zink, Appl. Spectroscopy, 1959, **13**, 94.

[40] A. J. Philcox, Spectrochimica Acta, 1960, **16**, 384.

[41] Ilford thin film half-tone plates are suitable.

Developer. A general-purpose developer of high activity and producing moderate contrast[42].

Fixer. A rapid fixer based on ammonium thiosulphate and containing a "hardener"[43].

A.6 Procedure

A.6.1 *Preparation of the solution of the sample*

Weigh accurately about 0.20 g of the ash (Note 3) into the platinum crucible and add 1.2 ± 0.01 g of the fusion mixture (Note 4). Cover the crucible with the lid and heat over a Meker burner, gently at first, then raising the temperature to dull red heat. When the initial reaction has ceased, raise the temperature to 1 000–1 100 °C for a further 5 minutes to complete the decomposition. Swirl the crucible occasionally to ensure that all ash particles have been drawn into the melt. Allow to cool and inspect the melt; if it has not the appearance of a clear glass, fuse it again until decomposition of the sample is complete.

Add 20 ml of the reference standard solution and 7 drops of the hydrogen peroxide (Note 5). Keep the crucible covered until effervescence has ceased. Remove the lid, dissolve any of the melt adhering to the underside of the lid in 3–4 drops of the nitric acid (12 + 88) and wash it into the crucible with a further 5 ml of the acid. Using a mechanical stirrer, dissolve the melt at room temperature (Note 6).

A.6.2 *Recording of spectra*

With a new cup or disk electrode, record duplicate spectrograms of the solution. Use a new counter electrode for each exposure and the following conditions:

Spectrograph setting, to cover the range 2 550–3 850 Å.

Excitation, 15 kV r.m.s. uncontrolled condensed spark.

Electrode gap, 4 mm.

Capacitance, 0.005 μF.

Added inductance, nil-nominal inductance reduced to a minimum.

Slit dimensions, width 0.02 mm, height 1.5 mm.

Quartz condensing lens and source to slit distance. The focal length of the lens and the distance of the source from the slit shall be selected so that, with the lens placed as near as possible to and in front of the slit, a real image of the spark is formed at the collimating lens of the spectrograph.

Exposure. No prespark; the time of exposure (about 1 min) is selected to suit the characteristics of the source unit and spectrograph (Note 7).

Substitute the rotating sector shutter for the condensing lens and, using a slit height of 18 mm, record a spectrogram of the D.C. iron-carbon arc for the determination of the emulsion characteristics of the plate. Develop the plate to constant gamma[44], using random agitation. Fix it for twice the time taken for the disappearance of silver halide (Note 8) and dry it.

A.6.3 *Plate calibration*

The object of calibrating the plate is to enable relative intensities to be inferred from the observed densitometer galvanometer readings. A method of general applicability is as follows (but see Note 9):

From the rotating sector spectrogram of the iron-carbon arc, select three or more lines the steps of which, together cover the range of photographic densities from 0.02–1.4.

Adjust the sensitivity of the galvanometer so that full-scale deflection is obtained from the clear glass region between spectra near the weakest step of one of the selected lines. Measure the galvanometer deflection for every step of this line. Repeat this procedure for each line (Note 10).

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[42] Suitable developers include:
Ilford PFP, dilute (1 + 1)
Ilford ID2, dilute (1 + 2)
Kodak D2, dilute (1 + 2)

[43] "Hypam", "Ilford" and "Amfix" (May & Baker) used with the appropriate hardener are suitable.

[44] The times of development necessary are as follows:

Developer	Time
PFP 1 + 1	4 min
ID2 1 + 2	3 min
D2 1 + 2	3 min

From these combined observations, construct a graph relating galvanometer deflection to log relative intensity.

A.6.4 *Evaluation of the spectrum*

Table A.1 shows suitable line pairs for the seven elements which are determined by this method, their excitation potentials and the range of the percentage of each in the sample that can be dealt with. These ranges can be extended by a factor not greater than two by varying the sample weight, but keeping the amount of internal standard (chromium) constant.

With the densitometer galvanometer adjusted to give full scale deflection between spectra and near to the line being measured, observe the galvanometer deflection for each of the lines in Table A.1 (Note 10).

Determine the log relative intensity of each line by reference to the plate calibration graph and subtract the log relative intensity of the chromium line from that of the line of the ash constituent. The analysis of the sample is then obtained from each spectrum by reference to graphs for each element which relate this difference to percentage composition. Take the average of the results obtained from the duplicate exposures.

Table A.1 — Suitable line pairs

Element	Line pair	Excitation potential[a]	Range suitability — oxide in ash
	Å	volts	per cent
Si	SiI 2881.6 CrI 3021.6	5.1 5.1	5.0 – 60.0
Al	AlI 3082.2 CrI 3021.6	4.0 5.1	5.0 – 50.0
Fe	FeII 2755.7 CrII 2757.7	5.5 6.0	3.0 – 50.0
Ca	CaII 3179.4 CrII 3180.7	7.0 6.4	0.5 – 25.0
Mg	MgII 2802.7 CrII 2757.7	4.4 6.0	0.05 – 2.0
Mg	MgII 2798.0 CrII 2757.7	8.8 6.0	0.5 – 10.0
Ti	TiII 3349.0 CrII 3358.5	4.3 6.1	0.1 – 4.0
Mn	MnII 2593.7 CrII 2757.7	4.8 6.0	0.1 – 3.0

[a] A. N. Zaidal, V. K. Prokof'ev and S. M. Raiskii, *Tables of spectrum lines*, Pergammon Press, 1961.
C. Moore, *An ultraviolet multiplet table*, Circular 488, Sections 1 and 2, National Bureau of Standards, 1950; 1952.

A.7 Preparation of calibration graphs from simulated ash solutions

Calibration graphs are prepared from spectra resulting from solutions which simulate the composition of ashes (Note 11). They are prepared by fusing pure silica with the fusion mixture and adding known amounts of solutions of the other constituents, which have in turn been prepared from materials of adequate purity (Table A.2).

Prepare primary solutions of chromium (the reference standard) and each of the elements except silica as indicated in Table A.2.

Pipette into seven separate 100 ml graduated flasks the volumes of the primary solutions indicated in Columns 1 to 7 of Table A.3 and dilute each to 100 ml with the nitric acid (1 + 4); 10 ml of each of these stock solutions contains the quantities of the constituents, other than silica, present in 0.2 g of simulated ash of the composition shown in Table A.3, together with the reference standard.

Weigh accurately the required amount of silica (Table A.3) into the platinum crucible and add 1.2 ± 0.01 g of the fusion mixture. Fuse to dissolve the silica and cool. Add 10 ml of the appropriate stock solution. Wash off the lid of the crucible with the nitric acid (7 + 93), dilute the contents of the crucible to about 25 ml with more of this nitric acid and extract the melt as described in Clause **A.6.1**.

Record at least three spectrograms of each simulated ash solution, distributing them over the whole of a plate in order to minimize the effect of variations in the emulsion and other factors. Record also a stepped sector iron-carbon arc spectrogram for the determination of the characteristics of the plate, as described in Clause **A.6.3**.

Plot a calibration curve for each element, relating differences between the log relative intensities of constituent and chromium lines to log percentage of the constituent.

A.8 Tolerances

The repeatability of the results depends both on the constituent and on its concentration in the sample. Values for the coefficient of variation "k" for the various constituents of between 0.01 and 0.03 have been obtained and duplicate results would be expected to lie within 4kC where C is the percentage of the constituent in the sample.

Table A.2 — Pure materials and preparation of the primary solutions

Element	Source	Weight taken	Solvent	Volume
		g		ml
Si	Spectroscopically pure silica ignited at 1 100 °C	—	—	—
Al	99.99 per cent pure metal	5.2938	Dilute HNO_3 (1 + 4)	250
Fe	Spectroscopically pure metal	2.7970		100
Ca	Spectroscopically pure calcium carbonate dried at 105 °C	7.1375		100
Mg	Spectroscopically pure metal	0.2413		100
Ti	Potassium titanium oxalate[a] dried at 105 °C	1.7727		100
Mn	Manganese sulphate[a]	1.1699		100
Cr	Potassium dichromate[a] dried at 150 °C	15.000		500

[a] Analytical reagent quality.

Table A.3 — Data for preparation of standard ash solutions

Simulated ash number	**1**		**2**		**3**		**4**		**5**		**6**		**7**	
Standard solution	**Volume** (ml)	**Per cent**	**Volume** (ml)	**Per cent**	**Volume** (ml)	**Per cent**	**Volume** (ml)	**Per cent**	**Volume** (ml)	**Per cent**	**Volume** (ml)	**Per cent**	**Volume** (ml)	**Per cent**
Cr	40	—	40	—	40	—	40	—	40	—	40	—	40	—
Al_2O_3	15	30	7.5	15	10	20	17.5	35	12.5	25	16	32	20	40
Fe_2O_3	20	40	10	20	15	30	8	16	4	8	2	4	6	12
CaO	2	4	1.25	2.5	0.75	1.5	6	12	10	20	3	6	4	8
MgO	2	0.4	12.5	2.5	6	1.2	15	3	10	2	20	4	4	0.8
TiO_2	1.25	0.25	2.5	0.5	2	0.4	6.5	1.3	8	1.6	4	0.8	5	1.0
Mn_3O_4	0.5	0.1	1.0	0.2	2.5	0.5	4	0.8	6	1.2	2	0.4	3	0.6
	Weight (g)		**Weight** (g)		**Weight** (g)		**Weight** (g)		**Weight** (g)		**Weight** (g)		**Weight** (g)	
SiO_2	0.0300	15	0.0900	45	0.0700	35	0.0400	20	0.0600	30	0.0800	40	0.0500	25

NOTE 1 If the sample contains chromium, other elements, e.g. cobalt, nickel or molybdenum, may be used.

NOTE 2 A spark source is used to ensure maximum repeatability.

NOTE 3 If the ash has absorbed water or carbon dioxide it may be necessary to correct for the loss on ignition (see Clause **14.7**) or to re-ignite the sample at 800 °C for 1 hour before weighing.

NOTE 4 If desired, the scale of working may be reduced, using 25 mg of sample (weighed to 0.01 mg) in a 10 ml crucible and reducing the amounts of the various reagents, including the reference standard, proportionately.

NOTE 5 The addition of hydrogen peroxide assists solution of the manganese, titanium and iron. Highly ferruginous ashes will need further additions of hydrogen peroxide.

NOTE 6 Dissolution takes about 20 minutes. Because this is a ratio method there is no need to dilute the solution to any specified volume.

NOTE 7 The exposure time should be chosen so that the strongest lines normally encountered have a density of about 1.4. The same exposure time should always be used.

NOTE 8 When the total fixing time exceeds three minutes, renew the fixing solution.

NOTE 9 Where the portion used of the characteristic curve of the plate is straight, or can be straightened by the application of a function of density such as

$$P = \tfrac{1}{2}\log\left(\frac{d_0{}^2 - dd_0}{d^2}\right)$$

where d_0 = galvanometer deflection for the clear glass,

d = galvanometer deflection for the line.

the following alternative method of plate calibration can be used. It relies on the phenomenon that the relative intensities of a suitable group of iron lines (preferably members of a multiplet) is sensibly constant for any particular combination of spectrograph and excitation conditions.

Stepped sector spark spectra of iron are recorded on several plates using excitation conditions identical with those used for samples. The steps of each line shown in Table A.4 of one spectrum are measured and the characteristic curves of the function of density versus log relative exposure for each line are plotted. The intercepts on the log relative exposure axis of the ten parallel straight lines thus obtained are equal to the log relative intensities of the lines. This procedure is repeated for each spectrum and the mean relative intensities of the lines are calculated from the several individual values.

Table A.4 — Relative intensities of suitable iron lines

Wavelength	Typical relative intensity
Å	
2 783.7	8.30
2 793.9	1.39
2 799.3	1.00
2 812.5	0.15
2 819.3	0.19
2 823.3	0.69
2 827.4	0.43
2 828.6	1.09
2 831.6	0.73
2 835.5	2.57

A spark spectrum of iron is recorded together with the spectra of the samples. The apparent relative intensities of these ten lines are measured and plotted against the determined values. The slope of the straight line thus obtained is the contrast factor, gamma (γ), of the plate.

The relative intensity of any line can then be obtained from the relationship

f(density) = γ log relative intensity.

If the function $P = \tfrac{1}{2}\log\left(\frac{d_0{}^2 - dd_0}{d^2}\right)$ is used, it is convenient to tabulate the corresponding values of d and P for values of gamma at intervals of 0.05 between 1.00 and 1.30.

NOTE 10 Using the plates specified, no background correction is necessary.

NOTE 11 Calibration graphs may also be obtained by the use of chemically analysed coal ashes, mixed if necessary with ferric oxide and calcium carbonate to give a sufficiently wide range of composition.

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