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Methods for

Analysis and testing of coal and coke —

Part 9: Phosphorus in coal and coke

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Cooperating organizations

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Contents

Foreword

This British Standard is Part 9 of a series issued under the same number, BS 1016, dealing with methods for the analysis and testing of coal and coke; the other Parts are as follows.

- — *Part 1: Total moisture of coal;*
- — *Part 2: Total moisture of coke;*
- — *Part 3: Proximate analysis of coal;*
- — *Part 4: Moisture, volatile matter and ash in the analysis sample of coke;*
- — *Part 5: Gross calorific value of coal and coke;*
- — *Part 6: Ultimate analysis of coal;*
- — *Part 7: Ultimate analysis of coke;*
- — *Part 8: Chlorine in coal and coke;*
- — *Part 10: Arsenic in coal and coke;*
- — *Part 11: Forms of sulphur in coal;*
- — *Part 12: Caking and swelling properties of coal;*
- — *Part 13: Tests special to coke;*
- — *Part 14: Analysis of coal ash and coke ash;*
- — *Part 15: Fusibility of coal ash and coke ash;*
- — *Part 16: Reporting of results.*

The methods given in BS 1016 are specified for the analysis of coal or of coke or, in some instances, for the analysis of both coal and coke. It is expected that the methods given in this Part would also be applicable to the determination of phosphorus in manufactured smokeless fuels (other than coke) made by a conventional process, although no systematic survey has been made.

The revision of Part 9 has been undertaken to complete the introduction of metric units and to adopt a uniform presentation; no technical changes have been made. The method involving dry oxidation (ashing) of the sample is technically equivalent to one of the three methods specified in ISO 622, but the wet oxidation method has no counterpart in an ISO Standard.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 4, 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.

1 Scope

This Part of BS 1016 describes two methods for determining the amount of phosphorus in coal and coke.

2 References

The titles of the publications referred to in this standard are listed on the inside back cover.

3 Definitions

3.1
coke

the solid residue of the distillation of coal at high temperature (above 800 °C)

3.2
ash

the inorganic matter remaining after coal or coke has been incinerated to constant mass under standardized conditions

3.3
repeatability

the maximum acceptable difference between duplicate determinations carried out at different times in the same laboratory on the same analysis sample by the same operator using the same apparatus

3.4
reproducibility

the maximum acceptable difference between the mean of duplicate determinations carried out in one laboratory and the mean of duplicate determinations carried out in any other laboratory on representative samples taken from the same gross sample after the last stage of the reduction process

4 Introduction

Alternative procedures are described for taking the phosphorus into solution. It may be extracted from the coal ash or coke ash by acid, or the coal or coke may be submitted to a wet oxidation process that yields a solution containing all the phosphorus from the sample. After either procedure a blue coloration is produced in the solution by addition of a single reagent solution. The intensity of the blue coloration, which is proportional to the concentration of phosphorus, is measured optically.

5 Sample

The coal or coke used for the determination of phosphorus shall be the analysis sample having a top size not greater than 0.2 mm (ground to pass a 212 μm test sieve complying with the requirements of BS 410), taken and prepared in accordance with BS 1017-1 or BS 1017-2 as appropriate. The sample shall be thoroughly mixed, preferably by mechanical means, immediately before the determination.

6 Dry oxidation method

6.1 Principle. The carbonaceous matter is removed from the coal or coke by ashing in a muffle furnace and the phosphorus is extracted from the ash by treatment with hydrofluoric and sulphuric acids. The addition of a solution containing ammonium molybdate and ascorbic acid (a reducing agent) produces a molybdenum blue colour. The absorbance of the blue solution is proportional to the concentration of phosphorus present and is measured by means of a suitable optical instrument.

6.2 Special reagents. All reagents, unless otherwise specified, shall be of analytical reagent quality. Distilled or deionized water complying with the requirements of BS 3978 shall be used throughout.

6.2.1 *Hydrofluoric acid,* approximately 20N.

6.2.2 *Sulphuric acid,* approximately 10N.

6.2.3 *Ammonium molybdate solution,* 60 g/l.

6.2.4 *Ascorbic acid solution,* 50 g/l, prepared fresh daily.

6.2.5 *Antimony potassium tartrate solution.* Dissolve 0.34 g in 250 ml of water.

6.2.6 *Reagent solution.* Mix 25 ml of the sulphuric acid (see **6.2.2**), 10 ml of the ammonium molybdate solution (see **6.2.3**), 10 ml of the ascorbic acid (see **6.2.4**) and 5 ml of the antimony potassium tartrate solution (see **6.2.5**). Prepare fresh immediately before use.

6.2.7 *Standard phosphorus solution.* Dissolve 0.4392 g of potassium dihydrogen orthophosphate (dried at 110 °C for 1 h) in water and dilute to 1 000 ml.

6.2.8 *Working standard phosphorus solution.* Dilute 10 ml of the standard phosphorus solution (see **6.2.7**) to 1 000 ml with water. 1 ml of this solution contains 1 μg of phosphorus. Prepare fresh before use.

6.3 Special apparatus. The following special apparatus is required.

6.3.1 *Muffle furnace,* as specified in BS 1016-3 or BS 1016-4.

6.3.2 *Silica dish,* as specified in BS 1016-3 or BS 1016-4. For low ash samples it may be more convenient to use a larger silica dish, for example 150 mm × 80 mm × 10 mm, for ashing.

6.3.3 *Platinum crucible,* 25 ml to 30 ml capacity, with lid.

6.3.4 *Hot air bath*[1)].

6.3.5 *A spectrophotometer or photoelectric absorptiometer* of the required sensitivity[2)].

6.4 Procedure. Determine the percentage of ash in the coal or coke sample as described in BS 1016-3 or BS 1016-4 as appropriate. The ash residue may be used for the determination of phosphorus. Alternatively, if the ash content is low, the preparation of the ash may be carried out in a larger silica dish (see **6.3.2**) but the depth of the sample should not exceed that specified in Part 3 or Part 4 of this standard.

Grind the ash in an agate mortar to pass a 63 μm sieve complying with the requirements of BS 410.

Weigh accurately about 0.05 g of ash into a platinum crucible. Add 2.0 ml of the sulphuric acid and about 2 ml of the hydrofluoric acid. Place the lid on the crucible and digest on a water bath for 30 min in a well ventilated fume cupboard. Remove and rinse the lid, collecting the washings in the crucible. 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 a few minutes. Allow to cool and add 0.5 ml of the sulphuric acid. Evaporate to fumes of sulphuric acid, heat for a few minutes and allow to cool (see note 1).

Add about 20 ml of water to the crucible and digest on the water bath for 30 min, when all the extract should be in solution. Allow to cool, transfer the solution to a 100 ml one-mark volumetric flask complying with the requirements of BS 1792 and dilute with water to 100 ml (solution A).

Prepare a blank solution exactly as described above but omitting the sample.

Pipette 10 ml of sample solution (the aliquot portion taken may be varied according to the phosphorus content of the sample), 10 ml of the blank solution and 10 ml of the working standard solution into separate 50 ml one-mark volumetric flasks complying with the requirements of BS 1792 (see note 2). A fourth 50 ml flask is required for the reagent blank. Pipette 5 ml of the reagent solution into each flask, swirling the contents during the addition, dilute with water to 50 ml and mix thoroughly. Allow to stand for 20 min and measure the absorbance of the solutions against water, in the spectrophotometer, using 40 mm cells at a wavelength of 710 nm or in the photoelectric absorptiometer, fitted with an appropriate filter[3)].

NOTE 1 Do not allow the contents of the crucible to evaporate completely to dryness at any stage.

NOTE 2 Calibration is linear for aliquot portions containing up to 30 μg of phosphorus. With high phosphorus coals or cokes it may be necessary to take a smaller aliquot.

6.5 Calculation of result

$$P = \frac{A(D_1 - D_2)}{1000\ Vm\ (D_3 - D_4)}$$

where

A is the percentage of ash in the analysis sample

m is the mass of the ash taken (in g)

V is the volume of sample solution taken for colour development (in ml)

D_1 is the absorbance of sample solution

D_2 is the absorbance of sample blank solution

D_3 is the absorbance of standard solution

D_4 is the absorbance of reagent blank solution

P is the percentage of phosphorus in the analysis sample

7 Wet oxidation method

7.1 Principle. The carbonaceous matter is removed from the coal or coke and the phosphorus is taken into solution by repeated oxidation with nitric acid in the presence of sulphuric acid. The phosphorus in the solution is determined in the same manner as with the dry oxidation method.

7.2 Special reagents. All reagents, unless otherwise specified, shall be of analytical reagent quality. Distilled or deionized water complying with the requirements of BS 3978 shall be used throughout.

[1)] A suitable air bath is described in DSIR. *Fuel Research Survey Paper* No. 50, Page 8 (HMSO, 1949).

[2)] A Hilger "Spekker" absorptiometer, Unicam SP 600 spectrophotometer or similar instrument is suitable.

[3)] An Ilford Type 609 filter (Spectrum deep red) is suitable.

7.2.1 *Sulphuric acid, d* = 1.84.

7.2.2 *Nitric acid, d* = 1.42.

7.2.3 *Ammonium molybdate solution,* 60 g/l.

7.2.4 *Ascorbic acid solution,* 50 g/l, prepared fresh daily.

7.2.5 *Antimony potassium tartrate solution.* Dissolve 0.34 g in 250 ml of water.

7.2.6 *Reagent solution.* Mix 25 ml of the sulphuric acid (see **7.2.1**), 10 ml of the ammonium molybdate solution (see **7.2.3**), 10 ml of the ascorbic acid solution (see **7.2.4**) and 5 ml of the antimony potassium tartrate solution (see **7.2.5**). Prepare fresh immediately before use.

7.2.7 *Standard phosphorus solution.* Dissolve in water 0.4392 g of potassium dihydrogen orthophosphate (dried at 110 °C for 1 h) and dilute to 1 000 ml.

7.2.8 *Working standard phosphorus solution.* Dilute 10 ml of the standard phosphorus solution (see **7.2.7**) to 1 000 ml with water. 1 ml of this solution contains 1 ml of phosphorus. Prepare fresh before use.

7.3 Special apparatus. A suitable apparatus constructed of borosilicate glass is shown assembled in Figure 1. It consists of the following items.

7.3.1 *Flask.* A Kjeldahl flask of 300 ml capacity fitted with a 24/29 ground glass socket complying with the requirements of BS 572.

7.3.2 *Fume duct.* A fume duct of approximately 28 mm outside diameter, fitted with a dropping funnel of at least 15 ml capacity and a 24/29 ground glass cone, complying with the requirements of BS 572. The fume duct may be of one piece or assembled from separate units by means of ground glass joints.

7.3.3 *Fume extractor.* A glass tube of approximately 40 mm diameter, sealed at one end and drawn out at the other end to form a connection to the water pump. The tube is fitted with a drain stopcock and a series of lipped holes to accommodate a number of fume ducts.

7.3.4 *Digestion rack.* A rack to hold the Kjeldahl flask at an angle of 45° over a bunsen burner, with a holder for the fume extractor.

7.3.5 *Glass water jet-pump or other suction device.*

7.4 Procedure for digestion of sample. Weigh accurately about 1 g of the coal or coke and transfer to the clean, dry Kjeldahl flask. Assemble the apparatus, as shown in Figure 1, in a well ventilated fume cupboard. Add 7 ml of the sulphuric acid and 3.5 ml of the nitric acid by means of the dropping funnel, rotating the flask so as to wash down any sample remaining in the neck.

After the initial reaction has subsided (see note 1) heat the flask carefully so that the reaction proceeds smoothly and without frothing. Continue heating the flask under the same conditions until only fumes of sulphuric acid are evolved. Add 0.2 ml to 0.4 of the nitric acid to the dropping funnel and run the acid drop by drop into the flask.

Heat for 2 min to 3 min until no more dense brown fumes are evolved. Add, in a similar manner, a further 0.2 ml to 0.4 ml of the nitric acid and heat again until brown fumes cease to be evolved. Continue such additions of nitric acid, heating in the same way after each addition, until all visible carbonaceous matter has been oxidized, rotating the flask periodically to wash down any carbonaceous matter adhering to the sides of the flask. After about 1½ h to 2 h the reaction mixture should be a pale greenish-yellow colour (see note 2) with no visible carbonaceous matter present.

Heat the flask more strongly until white fumes appear and allow to fume for 5 min (see note 3). Cool the flask to approximately room temperature, remove the dropping funnel and fume duct assembly and add a few glass beads to the contents of the flask.

Add cautiously 10 ml of water, heat until white fumes appear and then allow to fume gently for 10 min. Cool the flask until the evolution of the white fumes ceases, add 0.2 ml of the nitric acid, reheat the flask and allow to fume for a further 10 min.

To ensure complete oxidation, cool the flask to approximately room temperature and repeat the procedure described in the proceeding paragraph.

Cool the flask to approximately room temperature, add 10 ml of distilled water, heat to fuming and allow to fume for 20 min. Finally, add 10 ml of water, heat to fuming, allow to fume for 10 min and cool.

Add about 20 ml of water to the flask and digest on the water bath for 30 min, when all the extract should be in solution. Filter the solution through a hardened, acid-washed filter paper[4], allow to cool, transfer to a 100 ml one-mark volumetric flask complying with the requirements of BS 1792 and dilute with water to the mark (solution B). Prepare a blank solution in the same way omitting the sample.

Pipette 10 ml of solution B into a 50 ml conical flask and proceed as described in the last paragraph of **6.4** for the development of colour and subsequent measurement of the absorbance of the solutions.

NOTE 1 If violent frothing occurs on addition of the mixed acids, apply a damp cloth to the neck of the flask, and heat intermittently as the froth subsides.

NOTE 2 For the first 15 min of heating a coal sample, the reaction mixture is a tarry mass; subsequently it changes in colour from black to dark reddish-brown, to amber and finally to pale greenish-yellow. The time taken to reach this stage should not be more than 2 h. The carbonaceous matter remaining at this stage should be removed.

If a black liquid still remains after 45 min heating, either:

a) too low a temperature has been used and the nitric acid has not reacted with the sample; raise the temperature to distil off excess nitric acid, then continue the normal oxidation as described; or

b) too high a temperature has been used, nitric acid being distilled off without reacting; cool, add further nitric acid and heat the mixture as described.

Coke samples should also react to produce a clear greenish-yellow solution within 2 h, but certain exceptional samples may take longer.

NOTE 3 If the colour reverts to amber or deep red, add a further 0.2 ml to 0.4 ml of the nitric acid, heat to fuming and allow to fume for 5 min.

7.5 Calculation of result

$$P = \frac{D_1 - D_2}{10\ Vm\ (D_3 - D_4)}$$

where

m is the mass of the sample taken (in g)

V is the volume of sample solution taken for colour development (in ml)

D_1 is the absorbance of sample solution

D_2 is the absorbance of sample blank solution

D_3 is the absorbance of standard solution

D_4 is the absorbance of reagent blank solution

P is the percentage of phosphorus in the analysis sample

8 Reporting of result

The result, preferably the mean of duplicate determinations, shall be reported to the nearest 0.001 %.

9 Precision of the determination

When either of the two methods described in this Part of BS 1016 is operated satisfactorily the numerical values for repeatability and reproducibility (see clause **3**) should not exceed those given below; otherwise reference should be made to **4.4** in BS 1016-16:1971.

Phosphorus in coal or coke	**Repeatability**	**Reproducibility**
%		
Less than 0.02	0.002 absolute	0.005 absolute
Equal to or more than 0.02	10 % of the amount	25 % of the amount

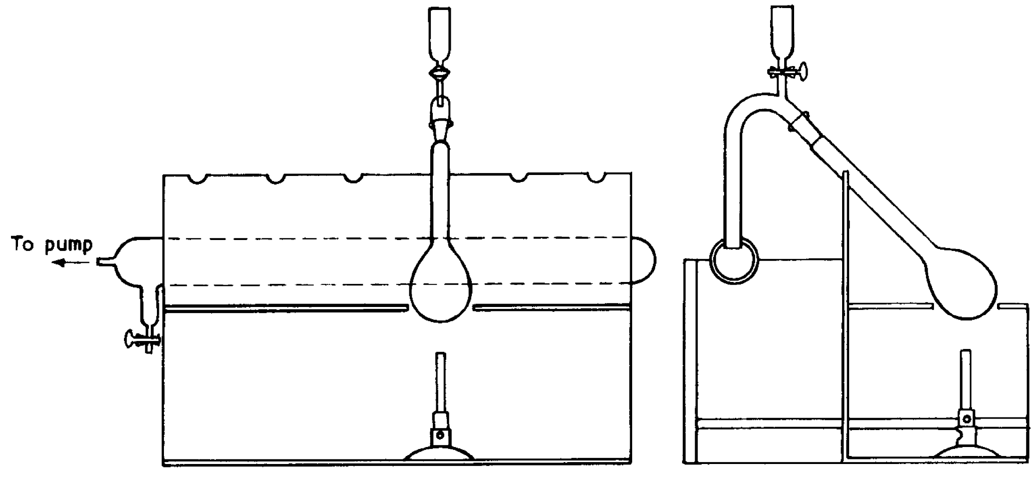

Figure 1 — Apparatus for the wet oxidation of the sample

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[4] Whatman No. 541 is suitable.

Publications referred to

BS 410, *Test sieves.*
BS 572, *Interchangeable conical ground glass joints.*
BS 1016, *Methods for the analysis of coal and coke.*
BS 1016-3, *Proximate analysis of coal.*
BS 1016-4, *Moisture, volatile matter and ash in the analysis sample of coke.*
BS 1016-16, *Reporting of results.*
BS 1017, *The sampling of coal and coke.*
BS 1017-1, *Sampling of coal.*
BS 1017-2, *Sampling of coke.*
BS 1792, *One-mark volumetric flasks.*
BS 3978, *Water for laboratory use.*
ISO 622, *Coal — Determination of phosphorus in ash.*

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