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Solid mineral fuels — Determination of phosphorus content — Reduced molybdophosphate photometric method

Combustibles minéraux solides — Dosage du phosphore — Méthode photométrique au molybdophosphate réduit

Reference number
ISO 622:2016(E)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 27, *Solid minerals fuels*, Subcommittee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 622:1981), which has been technically revised. This document incorporates changes related to references and other minor items following its systematic review.

Solid mineral fuels — Determination of phosphorus content — Reduced molybdophosphate photometric method

1 Scope

This document specifies a reduced molybdophosphate photometric method for the determination of the total phosphorus content of hard coal, lignites and coke. Two methods for taking the phosphorus into solution are specified, namely extraction from the coal or coke ash with acid or by repeated oxidation of the coal or coke, by acid, to remove carbonaceous matter.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 383, *Laboratory glassware — Interchangeable conical ground joints*

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

ISO 1171, *Solid mineral fuels — Determination of ash*

ISO 18283, *Hard coal and coke — Manual sampling*

3 Terms and definitions

No terms and definitions are defined in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

4.1 Extraction

Method 1: Removal of carbonaceous material by ashing in a muffle furnace under specified conditions, and extraction of phosphorus by treatment with hydrofluoric and sulphuric acids.

Method 2: Removal of carbonaceous material by repeated oxidation with nitric acid in the presence of sulphuric acid.

4.2 Determination

Addition of ammonium molybdate and ascorbic acid solution to the acid solution. Measurement of the absorbance of the resulting blue solution by a suitable optical instrument.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 Hydrofluoric acid, approximately 400 g/l solution.

WARNING — Aqueous hydrofluoric acid is a highly corrosive liquid which attacks glass; the vapour is irritant and toxic. Its action on the skin and eyes is strongly corrosive, producing severe and painful burns which may not be immediately evident and which respond slowly to treatment. The solution should be handled only inside a well-ventilated fume cupboard. In the event of contact or suspected contact, flood with water and seek immediate medical attention. The manufacturer's literature should be consulted for further information.

5.2 Sulphuric acid, approximately 490 g/l solution.

5.3 Sulphuric acid, concentrated, ρ 1,84 g/ml, approximately 98 % (m/m) solution.

5.4 Nitric acid, concentrated, ρ 1,42 g/ml, approximately 70 % (m/m) solution.

5.5 Ammonium molybdate, 60 g/l solution.

5.6 Ascorbic acid, 50 g/l solution.

Prepare the solution fresh daily.

5.7 Antimony potassium tartrate ($KSbO \cdot C_4H_4O_6$), 1,36 g/l solution.

5.8 Reagent solution.

Mix 25 ml of the sulphuric acid solution (5.2), 10 ml of the ammonium molybdate solution (5.5), 10 ml of the ascorbic acid solution (5.6) and 5 ml of the antimony potassium tartrate solution (5.7). Prepare fresh immediately before use.

5.9 Phosphorus, standard stock solution corresponding to 0,100 g of P per litre.

Weigh, to the nearest 0,000 1 g, 0,439 2 g of potassium dihydrogen monophosphate (KH_2PO_4) (dried at 110 °C for 1 h) and dissolve in water. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard stock solution contains 0,100 mg of P.

5.10 Phosphorus, standard working solution corresponding to 1 mg of P per litre.

Transfer 10 ml of the standard phosphorus solution (5.9) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix. Prepare fresh immediately before use.

1 ml of this standard working solution contains 1 µg of P.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Muffle furnace, as specified in ISO 1171.

6.2 Dish, of silica, porcelain or platinum, as specified in ISO 1171.

6.3 Insulating plate, of silica, 6 mm thick, or its equivalent, of such size as to be an easy sliding fit into the muffle furnace (6.1).

6.4 Platinum crucible, of capacity 25 ml to 30 ml, with lid.

6.5 Hot-air bath.

6.6 Digestion apparatus (see Figure 1), constructed of borosilicate glass, consisting of the following:

6.6.1 Flask, Kjeldahl flask, of capacity 300 ml, fitted with a 24/29 ground glass socket complying with ISO 383.

6.6.2 Fume duct, of outside diameter approximately 28 mm, fitted with a dropping funnel of capacity at least 15 ml and a 24/29 ground glass cone complying with ISO 383. The fume duct may be of one piece or assembled from spate units by means of ground glass joints.

6.6.3 Fume extractor, comprising a glass tube of diameter approximately 40 mm, 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.

6.7 Spectrophotometer, or **photoelectric absorptiometer**, of the required sensitivity.

7 Sample preparation

The sample of coal or coke shall be the analysis sample, ground to pass a 212 µm test sieve complying with the requirements of ISO 565, taken and prepared in accordance with ISO 18283. The sample shall be thoroughly mixed, preferably by a mechanical means, immediately before the determination.

8 Procedure

8.1 Dry oxidation method

8.1.1 Determine the percentage of ash in the coal or coke as specified in ISO 1171. Grind the ash in an agate mortar to pass a 63 µm sieve complying with ISO 565.

8.1.2 Weigh, to an accuracy of 0,1 mg, about 0,05 g of the ash into the platinum crucible (6.4).

8.1.3 Add 2,0 ml of the sulphuric acid solution (5.2) and about 2,0 ml of the hydrofluoric acid solution (5.1). Place the lid on the crucible and digest on a boiling 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.

8.1.4 Transfer the crucible to the hot-air bath (6.5), evaporate until dense white fumes from the sulphuric acid have evolved for a few minutes. Allow to cool, add 0,5 ml of the sulphuric acid solution (5.2), heat for a few minutes and allow to cool.

NOTE It is essential that the contents of the crucible are not evaporated completely to dryness at any stage.

8.1.5 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 one solution. Allow to cool, transfer the solution to a 100 ml one-mark volumetric flask and dilute with water to the mark (solution A).

If the sample has a high arsenic content, this can interfere with the result and the solution should be reduced before the phosphorus determination.

8.1.6 Prepare a blank solution exactly as described above, but omitting the coal or coke ash.

8.2 Wet oxidation method

8.2.1 Weigh, to an accuracy of 1 mg, about 1 g of the coal or coke sample.

8.2.2 Transfer the test portion (8.2.1) to the clean, dry Kjeldahl flask (6.6.1). Assemble the apparatus (6.6) as shown in Figure 1, in a well-ventilated fume cupboard. Add 7 ml of the sulphuric acid (5.3) and 3,5 ml of the nitric acid (5.4) by means of the dropping funnel, rotating the flask so as to wash down any sample remaining in the neck.

8.2.3 After the initial reaction has subsided, 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 ml of the nitric acid (5.4) to the dropping funnel and run the acid, drop by drop, into the flask.

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

8.2.4 Heat for 2 min to 3 min until no more dense brown fumes are evolved. Repeat the addition of the nitric acid and the heating, rotating the flask periodically to wash down any carbonaceous matter adhering to the sides of the flask, until all visible carbonaceous matter has been oxidized and the solution is a pale greenish-yellowish colour. This may take 1 1/2 h to 2 h, or even longer in exceptional cases with some coke samples.

NOTE For the first 15 min of heating a coal sample, the reaction mixture is a tarry mass; subsequently, it changes its colour from black to dark reddish-brown, to amber, and finally to a pale greenish-yellow. 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 more nitric acid and heat the mixture as described.

8.2.5 Heat the flask more strongly until white fumes appear and allow to fume for 5 min. 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.

NOTE 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.

8.2.6 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.

8.2.7 To ensure complete oxidation, cool the flask to approximately room temperature and repeat the procedure described in 8.2.5.

8.2.8 Cool the flask to approximately room temperature, add 10 ml of water, heat to fuming and allow to fume for 20 min. Add a further 10 ml of water, heat to fuming, allow to fume for 10 min and cool.

8.2.9 Add a further 20 ml of water to the flask and digest on the boiling water bath for 30 min, when all the extract should be in solution. Filter the solution through a hardened, acid-washed filter paper, allow to cool, transfer the filtrate to a 100 ml one-mark volumetric flask and dilute with water to the mark (solution B) (see the note in 8.1.5).

8.2.10 Prepare a blank solution exactly as described above, but omitting the coal or coke sample.

8.3 Determination

8.3.1 Pipette 10 ml of solution A or B as appropriate (see 8.1.5 or 8.2.9) (the aliquot portion taken may be varied according to the phosphorus content of the sample), 10 ml of the blank solution (see 8.1.6 or 8.2.10 as appropriate) and 10 ml of the standard solution (5.10) into separate 50 ml one-mark volumetric flasks. A fourth 50 ml flask is required for the reagent blank.

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 portion.

8.3.2 Pipette 5 ml of the reagent solution (5.8) into each flask, swirling the contents during the addition, dilute with water to the mark, and mix thoroughly. Allow to stand for 20 min.

8.3.3 Measure the absorbance of the solutions against water, in the spectrophotometer (6.7) using 40 mm cells at a wavelength of 710 nm or in the photoelectric absorptiometer fitted with an appropriate filter.

9 Expression of results

9.1 Method of calculation and formulae

Calculate the percentage of phosphorus (P) in the analysis sample, using Formulae (1) and (2).

a) Dry oxidation method (see 8.1):

$$\frac{A\left(D_1 - D_2\right)}{1\,000\,Vm\left(D_3 - D_4\right)} \tag{1}$$

where

A is the percentage of ash in the analysis sample;

m is the mass, in grams, of ash taken;

V is the volume, in millilitres, of sample solution taken for colour development;

D_1 is the absorbance of the sample solution;

D_2 is the absorbance of the sample blank solution;

D_3 is the absorbance of the standard phosphorus solution (5.10);

D_4 is the absorbance of the reagent blank solution.

b) Wet oxidation method (see 8.2):

$$\frac{\left(D_1 - D_2\right)}{10\ Vm\left(D_3 - D_4\right)} \tag{2}$$

where

m is the mass, in grams, of the test portion;

V, D_1, D_2, D_3 and D_4 have the same meaning as in a) above.

Report the result, preferably the mean of duplicate determinations, to the nearest 0,001 %.

10 Precision of the method

10.1 Repeatability

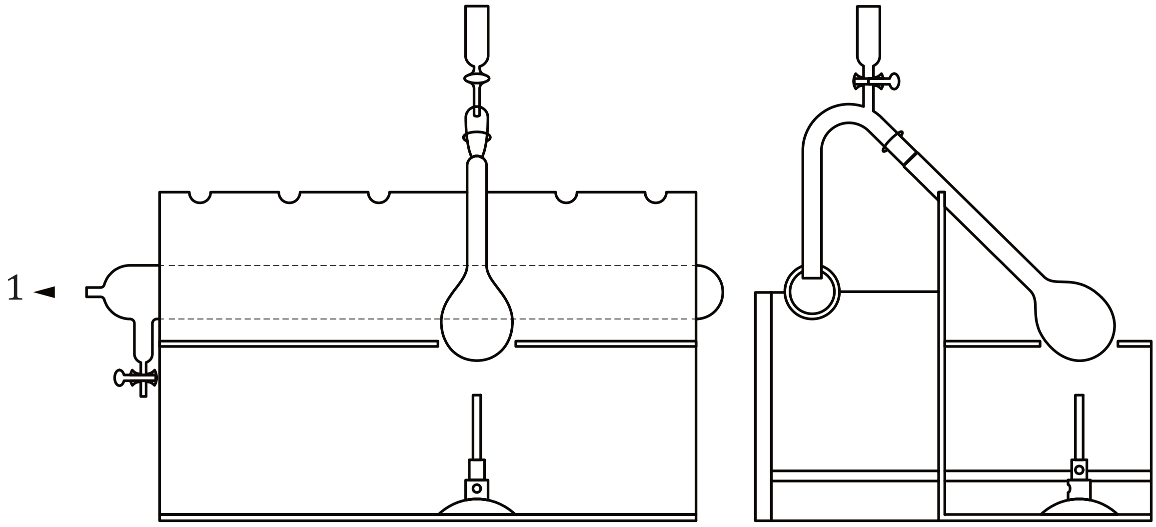
The results of duplicate determinations, carried out at different times in the same laboratory by the same operator with the same apparatus on two representative portions taken from the same sample (see Clause 7), should not differ by more than the values given in Table 1.

10.2 Reproducibility

The means of the results of duplicate determinations, carried out in two different laboratories on representative portions taken from the same sample (see Clause 7), should not differ by more than the values given Table 1.

Table 1

Phosphorus content of coal or coke % (m/m)	Repeatability	Reproducibility
Less than 0,02	0,002 absolute	0,005 absolute
Equal to or more than 0,02	10 % of the mean of the results	25 % of the mean of the results



Key

1 to pump

Figure 1 — Apparatus for wet oxidation of the sample

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