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Brown coals and lignites — Determination of humic acids

Charbons bruns et lignites — Dosage des acides humiques

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 5073 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This third edition cancels and replaces the second edition (ISO 5073:1999), of which this constitutes a minor revision.

Introduction

In this International Standard, humic acids are determined by the volumetric method with titration of extracts.

The test is empirical and, in order to ensure producible results, it is essential that the composition of the extraction solution, the temperature and the time of extraction be carefully controlled. The value 0,59, which is the average ratio of carbon content of humic acids for many brown coals and lignites, has been proved to be applicable. Another value may also be used, predetermined as described in Annex A, and applicable to different countries or locations.

Brown coals and lignites — Determination of humic acids

1 Scope

This International Standard specifies volumetric methods for the determination of

a) total humic acids, and

b) free humic acid,

of brown coals and lignites.

2 Normative references

The following referenced documents are indispensable for the application 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 1171, *Solid mineral fuels — Determination of ash*

ISO 1213-2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

ISO 5068-2, *Brown coals and lignites — Determination of moisture content — Part 2: Indirect gravimetric method for moisture in the analysis sample*

ISO 5069-2, *Brown coals and lignites — Principles of sampling — Part 2: Sample preparation for determination of moisture content and for general analysis*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1213-2 and the following apply.

3.1
humic acids
group of complex organic, amorphous compounds of high relative molecular mass which occur as free acid and as metal salts (humates)

3.2
total humic acids
humic acids extracted by an alkaline sodium pyrophosphate solution

3.3
free humic acid
humic acid extracted by a sodium hydroxide solution

4 Principle

4.1 Total humic acids

Extraction of an analysis sample of coal is carried out with an alkaline sodium pyrophosphate solution. Carbon in the humic acid extracts is oxidized with potassium dichromate followed by titration of the excess dichromate with ammonium ferrous sulfate standard solution.

4.2 Free humic acid

Extraction of an analysis sample of coal is carried out with a sodium hydroxide solution. Carbon in the humic acid extracts is oxidized with potassium dichromate followed by titration of the excess dichromate with ammonium ferrous sulfate standard solution.

5 Reagents

5.1 Sodium pyrophosphate, alkaline extraction solution.

Dissolve 15 g of crystalline sodium pyrophosphate ($Na_4P_2O_7 \bullet 10H_2O$) and 7 g of sodium hydroxide in 1 l of water.

5.2 Sodium hydroxide solution.

Dissolve 10 g of sodium hydroxide in 1 l of water.

5.3 Potassium dichromate standard solution, $c(1/6\ K_2Cr_2O_7) = 0{,}1$ mol/l.

Dissolve 4,903 6 g of potassium dichromate, previously dried at 130 °C, in water. Transfer to a 1 l volumetric flask and dilute to the mark with water.

5.4 Potassium dichromate oxidizing solution, $c(1/6\ K_2Cr_2O_7) = 0{,}4$ mol/l.

Dissolve 20 g of potassium dichromate in 1 l of water.

5.5 Ammonium ferrous sulfate titration solution, $c[(NH_4)_2Fe(SO_4)_2] = 0{,}1$mol/l.

Dissolve 40 g of ammonium ferrous sulfate in 1 l of water. Add 20 ml of concentrated sulfuric acid. Store in a dark bottle.

Standardize the ammonium ferrous sulfate titration solution against the $c(1/6\ K_2Cr_2O_7) = 0{,}1$ mol/l potassium dichromate standard solution (5.3) for each batch of samples to be analysed.

Pipette 25 ml of potassium dichromate standard solution (5.3) into a 300 ml conical flask. Add 70 ml to 80 ml of water. Carefully add 10 ml of concentrated sulfuric acid and 3 drops of 1,10-phenantholine indicator. After cooling, titrate with the ammonium ferrous sulfate standard solution to a red colour.

Calculate the concentration, in moles per litre, of the ammonium ferrous sulfate solution as follows:

$$c = 0{,}1 \times 25/V$$

where

c is the concentration, expressed in moles per litre, of the ammonium ferrous sulfate solution;

V is the volume of ammonium ferrous sulfate solution required for the titration.

5.6 1,10-Phenanthroline indicator.

Dissolve 1,5 g of 1,10-phenanthroline and 1 g of ammonium ferrous sulfate in 100 ml of water. Store in a dark bottle.

5.7 Sulfuric acid, concentrated, $\rho_{20} = 1{,}84$ g/ml.

6 Apparatus

6.1 Water bath, thermostatically controlled to (100 ± 1) °C, with four holes at least.

6.2 Balance, sensitive to 0,1 mg.

7 Sample

Prepare the sample for the determination of humic acids in accordance with ISO 5069-2.

For calculation to a dry basis, the moisture in the analysis sample shall be determined according to ISO 5068-2.

8 Procedure

8.1 Extraction of total humic acids

Weigh (0,2 ± 0,000 2) g of analysis sample into a conical flask. Add 150 ml of alkaline sodium pyrophosphate extraction solution (5.1) and mix until the sample is thoroughly wetted. Place a small funnel on the flask and heat in the boiling water bath (6.1) for 2 h, shaking frequently to ensure precipitation of insoluble material.

Remove the flask from the water bath. Allow to cool to room temperature and quantitatively transfer the extract and residue to a 200 ml volumetric flask. Dilute to the mark with water and shake to ensure thorough mixing.

Determine the total humic acids ($w_{\mathrm{HA,t}}$) extracted by alkaline sodium pyrophosphate as specified in 8.3.

8.2 Extraction of free humic acid

Weigh (0,2 ± 0,000 2) g of analysis sample into a conical flask. Add 150 ml of sodium hydroxide extraction solution (5.2) and mix until the sample is thoroughly wetted. Place a small funnel on the flask and heat in the boiling water bath (6.1) for 2 h, shaking frequently to ensure thorough mixing.

Remove the flask from the water bath. Allow to cool to room temperature and quantitatively transfer the extract and residue to a 200 ml volumetric flask using water. Dilute to the mark with water and shake to ensure thorough mixing.

Determine the free humic acid ($w_{\mathrm{HA,f}}$) extracted by sodium hydroxide as specified in 8.3.

8.3 Determination of humic acids in extracts

8.3.1 Oxidation of extracts

Pipette 5 ml of clarified or dry-filtered extract into a 250 ml to 300 ml conical flask. Pipette 5 ml of potassium dichromate oxidizing solution (5.4) into the flask. Carefully add 15 ml of concentrated sulfuric acid (5.7). Place in the boiling water bath (6.1) and heat for 30 min. Allow to cool to room temperature. Dilute to approximately 100 ml.

8.3.2 Titration of extracts

Add 3 drops of 1,10-phenanthroline indicator (5.6) to the solution from 8.3.1 and titrate with the ammonium ferrous sulfate titration solution (5.5) to a brick red colour.

8.3.3 Blank

8.3.3.1 Blank for total humic acids

Pipette 5 ml of sodium pyrophosphate (5.1) into a 250 ml to 300 ml conical flask, add the potassium dichromate oxidizing solution (5.4) and the concentrated sulfuric acid as specified in 8.3.1 and carry out the titration as specified in 8.3.2.

8.3.3.2 Blank for free humic acids

Pipette 5 ml of sodium hydroxide (5.2) into a 250 ml to 300 ml conical flask, add the potassium dichromate oxidizing solution and the concentrated sulfuric acid as specified in 8.3.1 and carry out the titration as specified in 8.3.2.

9 Expression of results

Calculate the total humic acid content ($w_{\mathrm{HA,t}}$) or free humic acid content ($w_{\mathrm{HA,f}}$), as a percentage by mass, of the sample as analysed according to the following formula:

$$w_{\mathrm{HA}} = \frac{(V_0 - V_1) \times 0{,}003 \times c}{0{,}59 \times m} \times \frac{V_\mathrm{e}}{V_\mathrm{a}} \times 100$$

where

0,003	is the millimole mass of carbon, in grams per millimole;
V_0	is the volume of the ammonium ferrous sulfate titration solution used in the blank titre, in millilitres;
V_1	is the volume of the ammonium ferrous sulfate titration solution used in the extract titre, in millilitres;
c	is the concentration of the ammonium ferrous sulfate titration solution as determined in 5.5, in moles per litre;
V_e	is the volume of the extract, in millilitres;
V_a	is the volume of the aliquot taken for titration, in millilitres;
0,59	is the average ratio of carbon content of humic acids for brown coals and lignites (see the note below);
m	is the mass of the sample taken for the test, in grams.

NOTE For different countries or locations, the average ratio of carbon content of humic acids of brown coals and lignites can be checked or redetermined as specified in Annex A.

10 Precision of the method — Repeatability limit

The results of duplicate determinations, carried out on the same day in the same laboratory by the same operator with the same apparatus on the two separate test portions of the same sample, should not differ by more than the values given in Table 1.

Table 1 — Precision

Humic acid content	Repeatability limit
Up to 20 %	1 % (absolute)
Above 20 %	2 % (absolute)

11 Test report

The test report shall contain the following information:

a) a reference to this International Standard including year of publication;

b) the identification of the sample tested;

c) the result of the determination performed, together with the analysis basis;

d) any unusual feature noted during the determination.

Annex A
(normative)

Determination of the ratio of carbon content of humic acids of brown coals and lignites

A.1 Weigh about 10 g of analysis sample of brown coals and lignites into three or four conical flasks separately depending on the humic acid content of the sample (can yield 3 g or 4 g of humic acid sample). Pipette an appropriate amount of the alkaline sodium pyrophosphate extraction (5.1) into each conical flask equivalent to 150 ml per gram of the analysis sample and mix until the sample is thoroughly wetted. Place a small funnel on the flask and heat in the boiling water bath (6.1) for 2 h, shaking frequently to ensure precipitation of insoluble material.

A.2 Remove the flask from the water bath, cool to room temperature, centrifuge the contents of flasks for 5 min. Collect the solution in the beakers. Add (1 + 1) HCl to the solution until the humic acid is precipitated fully (pH 1 to pH 3 for the solution).

A.3 Centrifuge the suspension. Decant and discard the solution. Separate the residue through a medium-textured paper, wash the residue with water until peptization of the humic acids begins, which is indicated by the formation of a gel or colloid (pH 6 to pH 7 for the filtered solution).

A.4 Transfer the residue to the clear beakers or vessels and dry it at 105 °C to 110 °C. The dried residue is the humic acid sample.

A.5 Weigh 1 g, to the nearest 0,2 mg, of the humic acid sample (A.4) into a clear, dry dish and determine the ash according to ISO 1171. Calculate the humic acid content (w_{HA}) of the humic acid sample as follows:

$$w_{\mathrm{HA}} = 100 - w_{\mathrm{A}}$$

where w_{A} is the ash of the humic acid sample, in percent.

A.6 Weigh 0,1 g, to the nearest 0,2 mg, of the humic acid sample (see A.4) into a conical flask. Add 150 ml of the alkaline sodium pyrophosphate extraction solution (5.1). Shake to enable it to be dissolved fully. Transfer the contents of the flask to a 200 ml volumetric flask and dilute to the mark with water. Shake to ensure thorough mixing, then dry-filter through a medium-textured paper into a flask. Accurately pipette 5 ml of filtered solution into a 250 ml conical flask. Determine the carbon content of the humic acid sample as specified in 8.3.

Calculate the carbon content (w_{C}) of the humic acid sample according to the formula:

$$w_{\mathrm{C}} = \frac{(V_0 - V_1) \times 0{,}003 \times c}{m} \times \frac{V_{\mathrm{e}}}{V_{\mathrm{a}}} \times 100$$

where

0,003 is the millimole mass of carbon, in grams per millimole;

V_0 is the volume of the ammonium ferrous sulfate titration solution (5.5) used in the blank titre, in millilitres;

V_1 is the volume of the ammonium ferrous sulfate titration solution (5.5) used in the extract titre, in millilitres;

c is the concentration of the ammonium ferrous sulfate titration solution as determined in 5.5, in moles per litre;

V_e is the volume of the extract, in millilitres;

V_a is the volume of the aliquot taken for titration, in millilitres;

m is the mass of the humic acid sample taken for the test, in grams.

A.7 The ratio of carbon content of humic acid is calculated as follows:

$$R_C = \frac{w_C}{w_{HA}}$$

where

w_C is the carbon content of the humic acid sample, in percent (A.6);

w_{HA} is the humic acid content of the humic acid sample, in percent (A.5).

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