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Brown coals and lignites — Determination of humic acids

Charbons bruns et lignites — Dosage des acides humiques

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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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 of the voluntary nature of standards, 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 27, *Coal and Coke*, Subcommittee SC 5, *Methods of analysis*.

This fourth edition cancels and replaces the third edition (ISO 5073:2013), of which it constitutes a minor revision. The changes compared to the previous edition are as follows:

- referenced documents have been updated;
- terms and definitions have been added;
- sample has been added;
- determination of humic acids in extracts has been amended;
- calculation and expression of results have been amended;
- precision has been amended;
- test report has been amended;
- Annex A has been amended.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html

Introduction

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

The test is empirical and, in order to ensure reproducible 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 document specifies volumetric methods for the determination of total humic acids and free humic acid of brown coals and lignites.

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 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 13909-4, *Hard coal and coke — Mechanical sampling — Part 4: Coal — Preparation of test samples*

ISO 18283, *Coal and coke — Manual sampling*

3 Terms and definitions

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

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

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

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

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 (3.1) extracted by an alkaline sodium pyrophosphate solution

3.3
free humic acid
humic acid (3.1) 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 ($Na_4P_2O_7 \cdot 10H_2O$) 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 water. Add 20 ml of concentrated sulfuric acid and dilute to 1 l. 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 (5.7). Allow the solution to cool to ambient temperature, then add 3 drops of 1,10-phenantholine (5.6) indicator. 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 amount of substance concentration, expressed in moles per litre, of the ammonium ferrous sulfate solution;

V is the volume, in mL, 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, ρ_{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, with a resolution of 0,1 mg.

7 Sample

The sample shall be the general analysis test sample, prepared to a nominal top size of 212 µm by the preparation procedures specified in ISO 13909-4 or ISO 18283.

The sample should be brought in moisture equilibrium with the laboratory atmosphere by exposure in a thin layer on a tray. Exposure time shall be kept to a minimum.

The sample shall be thoroughly mixed immediately before analysis, preferably by mechanical means.

Duplicate determinations of moisture from the same test sample shall be conducted concurrently with the determination of the humic acids by the method specified in ISO 5068-2.

8 Procedure

8.1 Extraction of total humic acids

Transfer a (0,2 ± 0,000 2) g mass 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 water bath (6.1) with the temperature of (100 ± 1) °C 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. Filter with dry medium speed qualitative filter-paper. Discard the initial 10ml and collect the dry-filtered extract A of (50 to 100) ml for the determination of total humic acids.

Determine the total humic acids, $w_{\mathrm{HA,t}}$, extracted by alkaline sodium pyrophosphate as specified in 8.3.1.

8.2 Extraction of free humic acid

Transfer a (0,2 ± 0,000 2) g mass 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 water bath (6.1) with the temperature of (100 ± 1) °C 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. Filter with dry medium speed qualitative filter-paper. Discard the initial 10 ml, and collect the dry-filtered extract B of (50 to 100) ml for the determination of free humic acids.

Determine the free humic acid, $w_{\mathrm{HA,f}}$, extracted by sodium hydroxide as specified in 8.3.2.

8.3 Determination of humic acids in extracts

8.3.1 For total humic acids

8.3.1.1 Oxidation of extracts

Pipette 5 ml of dry-filtered extract A (8.1) 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 water bath (6.1) with the temperature of (100 ± 1) °C and heat for 30 min. Allow to cool to room temperature. Dilute to approximately 100 ml.

8.3.1.2 Titration of extracts

Add 3 drops of 1,10-phenanthroline indicator (5.6) to the solution from 8.3.1.1 and titrate with the ammonium ferrous sulfate titration solution (5.5) to a brick red colour.

8.3.1.3 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, heat, cool, and dilute, as specified in 8.3.1.1 and carry out the titration as specified in 8.3.1.2.

8.3.2 For free humic acids

8.3.2.1 Oxidation of extracts

Pipette 5 ml of dry-filtered extract B (8.2) 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) with the temperature of (100 ± 1) °C and heat for 30 min. Allow to cool to room temperature. Dilute to approximately 100 ml.

8.3.2.2 Titration of extracts

Add 3 drops of 1,10-phenanthroline indicator (5.6) to the solution from 8.3.2.1 and titrate with the ammonium ferrous sulfate titration solution (5.5) to a brick red colour.

8.3.2.3 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, heat, cool, and dilute, as specified in 8.3.2.1 and carry out the titration as specified in 8.3.2.2.

9 Calculation and expression of results

9.1 Calculate the total humic acid mass fraction, $w_{\mathrm{HA,t}}$, or free humic acid mass fraction, $w_{\mathrm{HA,f}}$, as a percent, of the sample as analysed according to Formula (1):

$$w_{\mathrm{HA,t}} / w_{\mathrm{HA,f}} = \frac{(V_0 - V_1) \times 0{,}003 \times c}{0{,}59 \times m} \times \frac{V_\mathrm{e}}{V_\mathrm{a}} \times 100 \qquad (1)$$

where

0,003 is the molar 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 amount of substance 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 (200 ml, as stated in 8.1 and 8.2), in millilitres;

V_a is the volume of the aliquot taken for titration (5 ml, as stated in 8.3.1.1 and 8.3.2.1), in millilitres;

0,59 is the average ratio of carbon mass fraction to humic acids mass fraction for brown coals and lignites (see the note below);

m is the mass of the sample taken for the test, in grams;

100 is conversion factor from dimensionless mass fraction to percent, in %.

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

10 Precision

10.1 Repeatability limit

The results of duplicate determinations, carried out in the same laboratory by the same operator with the same apparatus within a short interval of time on representative portions taken from the same analysis sample, shall not differ by more than the values of the repeatability limit, shown in Table 1.

Table 1 — Repeatability limit

Test parameter (air-dried basis) $w_{HA,t}/w_{HA,f}$ %	**Maximum acceptable differences between results** absolute, %
	Repeatability limit r
<20	1
≥20	2

11 Test report

The test report shall include the following information:

a) identification of the sample tested;

b) the method used by reference to this document, i.e. ISO 5073:2021;

c) the date of the determination;

d) the results and the method of expression used.