International Standard 5073

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Brown coals and lignites — Determination of humic acids

Charbons bruns et lignites — Dosage des acides humiques

First edition — 1985-07-15

UDC 662.642 : 543.8 : 547.992.2 **Ref. No. ISO 5073-1985 (E)**

Descriptors : minerals and ores, solid fuels, coal, lignite, chemical analysis, determination of content, humic acids.

Price based on 3 pages

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 5073 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*.

Printed in Switzerland

Brown coals and lignites — Determination of humic acids

1 Scope and field of application

This International Standard specifies methods for the determination of

a) total humic acids content, i.e. humic acids which are bonded with the mineral matter of coal as humates, and free humic acids;

b) free humic acids.

The humic acid content of brown coals and lignites varies with the type of coal and petrographic composition.

This International Standard applies to the scientific characterization of brown coal and lignites, and to their utilization, for example for briquetting and agriculture.

2 References

ISO 975, *Brown coals and lignites — Determination of the yield of toluene soluble extract.*[1]

ISO 1015, *Brown coals and lignites — Determination of moisture content — Direct volumetric method.*

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

ISO 5068, *Brown coals and lignites — Determination of moisture content — Indirect gravimetric method.*

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

3 Definitions

For the purpose of this International Standard, the following definitions apply.

3.1 humic acids: A group of amorphous condensed polycarboxylic acids of high relative molecular mass which occur as free humic acids and as salts (humates) of calcium, magnesium, iron, etc.

3.2 free humic acids: Humic acids obtained by a single stage extraction of coal with a 1 % (m/m) sodium hydroxide solution followed by precipitation with mineral acid.

3.3 total humic acid: Sum of the free humic acids and humic acids bonded as salts (humates) extracted by an alkaline sodium pyrophosphate solution followed by extraction with a 1 % (m/m) sodium hydroxide solution and precipitation with mineral acid.

4 Determination of total humic acids

4.1 Principle

Action of an alkaline solution of sodium pyrophosphate at ambient temperature on an analytical sample of coal from which bitumens have been removed; single stage extraction of the sample with a hot sodium hydroxide solution, precipitation of humic acids with an excess of mineral acid, and weighing of the precipitate.

NOTE — For the purpose of this International Standard, "bitumen" is synonymous with "toluene soluble extract" as determined in ISO 975.

4.2 Reagents

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

4.2.1 Toluene, ϱ_{20} = 0,867 g/ml, boiling range 110 to 111 °C. (At least 95 % should distil within this range.)

WARNING — Toluene is flammable and toxic by inhalation, ingestion or skin absorption.

4.2.2 Sodium hydroxide, 1 % (m/m) solution.

Dissolve 10 g of NaOH in water and make up to 1 000 ml.

4.2.3 Alkaline sodium pyrophosphate, solution.

Dissolve 44,6 g of crystalline sodium pyrophosphate decahydrate ($Na_4P_2O_7 \cdot 10H_2O$) and 4 g of sodium hydroxide in 100 ml water.

---

[1] At present at the stage of draft. (Revision of ISO 975-1975.)

4.2.4 Hydrochloric acid, 5 % (*V*/*V*).

4.3 Apparatus

Ordinary laboratory apparatus, and

4.3.1 Extraction apparatus, for bitumens separation (see ISO 975).

4.3.2 Drying oven, capable of being maintained at 90 ± 5 °C, or an **infra-red drying lamp.**

4.3.3 Centrifuge, capable of a minimum rate of rotation of 210 rad/s, with **centrifuge tubes** of at least 100 ml capacity.

NOTE — The RCF of the centrifuge should be sufficient to ensure separation of all precipitates or colloids from the corresponding solution.

4.3.4 Mechanical shaker.

4.3.5 Boiling water-bath.

4.3.6 Muffle furnace, capable of being maintained at 600 ± 25 °C.

4.4 Samples

Grind 10 to 15 g of the laboratory sample to pass a sieve of nominal size of openings 1 mm, according to the method specified in ISO 5069/2, and extract the bitumens using the method specified in ISO 975. Air dry the coal remaining after the extraction and again grind the test sample to pass a sieve of nominal size of openings 0,2 mm. Determine the moisture in accordance with the method specified in ISO 1015 and the ash in accordance with the method specified in ISO 1171. Record the values obtained.

NOTE — If the content of bitumens is lower than 3 % (*m*/*m*) (dry basis), the removal of bitumens may be omitted.

4.5 Procedure

4.5.1 Weigh out 1,0 g (equivalent to dry ash-free) of the test sample (4.4). If the expected yield of humic acids is less than 20 % (*m*/*m*), take double the amount of test sample. Put the test portion into a 250 ml conical flask A. Add 100 ml of the alkaline sodium pyrophosphate solution (4.2.3) and mix for 1 h using the mechanical shaker (4.3.4).

Centrifuge the suspension for 15 min at 210 rad/s (see 4.3.3). Decant the solution into a separate 1 litre conical flask B. Wash the undissolved residue twice with 100 ml of sodium hydroxide solution (4.2.2). Centrifuge after each washing, collecting the washings in conical flask B. Transfer the washed residue of the coal back to flask A. Add 100 ml of sodium hydroxide solution (4.2.2) and heat for 2 h on the boiling water-bath (4.3.5). After cooling to ambient temperature, centrifuge the contents of flask A for 15 min at 210 rad/s (see 4.3.3). Decant the solution into flask B. Wash the undissolved residue twice with 100 ml of sodium hydroxide solution (4.2.2). Centrifuge after each washing, collecting the washings in flask B.

NOTE — The extraction of humic acids should be complete within 7 h.

4.5.2 Filter the contents of flask B into a 1 litre volumetric flask and make up to the mark. Pipette 100 ml of the filtrate into a beaker and add 60 ml of hydrochloric acid (4.2.4) to precipitate the humic acids. Centrifuge the suspension. Decant the solution. Wash the residue with water. Repeat the washing operation until peptization of the humic acids begins, which is indicated by the formation of a gel or colloid. Add 5 ml of hydrochloric acid (4.2.4) to the colloidal solution to precipitate the humic acids once again.

Separate the resulting precipitate from the liquid by filtration through an ashless filter paper, previously dried to constant mass in the drying oven (4.3.2) at 90 ± 5 °C. Transfer the filter paper to a weighing bottle which has been heated to constant mass in the drying oven (4.3.2) at 90 ± 5 °C. Dry the bottle and precipitate at a temperature of 90 ± 5 °C for 1 h. Remove the bottle from the oven, cool initially for 5 min in air then in a desiccator containing a suitable desiccant, and weigh. Repeat the drying, cooling and weighing procedures until the results of two successive weighings do not differ by more than 0,000 1 g. Record the mass.

Transfer the precipitate and the filter paper to a crucible which has been heated to constant mass in the muffle furnace (4.3.6) at a temperature of 600 ± 25 °C. Ignite the crucible and its contents at a temperature of 600 ± 25 °C for 1 to 2 h. Remove the crucible from the furnace, cool, initially for 5 min in air and then in a desiccator containing a suitable desiccant, and weigh. Repeat the heating, cooling and weighing procedures until the results of two successive weighings do not differ by more than 0,000 1 g. Record the mass.

5 Determination of free humic acids

5.1 Principle

Single stage extraction of the coal sample, after removal of bitumens, with a 1 % (*m*/*m*) sodium hydroxide solution, precipitation of humic acids with excess mineral acid, and weighing of the precipitate. (See the note to 4.1.)

5.2 Reagents

See 4.2.

5.3 Apparatus

See 4.3.

5.4 Samples

See 4.4.

5.5 Procedure

Weigh out 2,0 g (equivalent to dry ash-free) of the test sample (4.4). Put the test portion into a 250 ml conical flask A. Add 100 ml of sodium hydroxide solution (4.2.2). Heat for 2 h on the boiling water-bath (4.3.5). After cooling to ambient temperature, centrifuge the contents of flask A for 15 min at

210 rad/s (see 4.3.3). Decant the solution into a separate 500 ml conical flask B. Wash the undissolved residue twice with 100 ml of sodium hydroxide solution (4.2.2). Centrifuge after each washing, collecting the washings in flask B.

Filter the alkaline solution from flask B into a 500 ml volumetric flask. Make up to the mark. Pipette 100 ml of the alkaline solution into a beaker, add 60 ml of hydrochloric acid (4.2.4) and proceed as in 4.5.2.

6 Expression of results

Calculate the percentage by mass of total humic acids content or free humic acids content on the dry ash-bitumen-free (HA^{dabf}) basis according to the formula

$$\frac{100\,V\,(m_1 - m_2)}{V_1 m}$$

where

m_1 is the mass, in grams, of dry humic acids;

m_2 is the mass, in grams, of ash residue of humic acids;

V is the total volume, in millilitres, of alkaline solution;

V_1 is the aliquot part, in millilitres, of alkaline solution;

m is the mass, in grams, of coal taken, on a dry ash-bitumen-free basis, calculated according to the equation

$$m = m_3 \left(\frac{100 - w_W^a - w_A^a}{100} \right)$$

in which

m_3 is the mass, in grams, of coal, free from bitumens, taken for the analysis;

w_W^a is the moisture content, expressed as a percentage by mass, in the sample of coal, free from bitumens;

w_A^a is the ash value, expressed as a percentage by mass, in the sample of coal, free from bitumens.

Give the results to the nearest 0,1 % (m/m).

7 Precision of the method

Table

Total humic acids and free humic acids	**Maximum acceptable difference between duplicate results obtained**	
	Within laboratory (Repeatability)	**Between laboratories** (Reproducibility)
Up to 20 %	10 % of the lower result	20 % of the lower result
Above 20 %	5 % of the lower result	10 % of the lower result

7.1 Repeatability

The results of duplicate determinations carried out at different times in the same laboratory, by the same operator, with the same apparatus, on the same analysis sample, should not differ by more than the value given in the table.

7.2 Reproducibility

The means of the results of duplicate determinations carried out in each two laboratories, on representative portions taken from the same sample after the last stage of sample preparation, should not differ by more than the value given in the table.

8 Test report

The test report shall contain the following information:

a) the reference of the method used;

b) the result and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

This page intentionally left blank