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Coal and coke — Determination of total sulfur by Coulomb titration method

Charbon et coke — Détermination de la teneur totale en soufre par la méthode de titrage de Coulomb

Reference number
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Foreword

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

This second edition cancels and replaces the first edition (ISO 20336:2017), which has been technically revised.

The main changes are as follows:

- replaced “solid mineral fuels” with “coal and coke” and “content” with “mass fraction”;
- added Figure 2 of a purified air stream supply system;
- added a note to 8.1.4.

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

The objective of this document is to provide an alternative method for determining the total sulfur mass fraction in coal and coke with high-temperature combustion by Coulomb titration using automated instruments.

Coal and coke — Determination of total sulfur by Coulomb titration method

1 Scope

This document specifies an alternative method of determining the total sulfur mass fraction of coal and coke by high-temperature combustion by Coulomb titration.

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 687, *Coke — Determination of moisture in the general analysis test sample*

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

ISO 11722, *Solid mineral fuels — Hard coal — Determination of moisture in the general analysis test sample by drying in nitrogen*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology 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/

4 Principle

In the presence of the catalyst, a sample of known mass is combusted at 1 150 °C in a stream of purified air. The sulfur oxides are formed and dissolved in the electrolytic solution. The sulfur dioxides are titrated by the iodine and bromine librated from the electrolysis of the potassium iodide and potassium bromide solution. The quantity of the electricity consumed by electrolysis is integrated and used to calculate the mass fraction of sulfur dioxides. The instrument is calibrated with certified reference materials. The percentage of total sulfur in the sample is calculated according to the sulfur dioxides mass fraction and the prior calibration.

5 Reagent and materials

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

5.1 Potassium iodide.

5.2 Potassium bromide.

5.3 Glacial acetic acid.

5.4 Self-indicating silica gel, industrial grade.

5.5 Sodium hydroxide, chemical grade.

5.6 Electrolytic solution, composed of 5 g of potassium iodide (5.1) and 5 g of potassium bromide (5.2) dissolved in (250 to 300) ml of water, then add 10 ml of glacial acetic acid.

5.7 Glass wool.

5.8 Aluminosilicate wool.

5.9 Catalyst, tungsten trioxide.

5.10 Certified reference materials (CRMs), coal or coke.

6 Apparatus

6.1 Instrument, for determining sulfur by Coulomb titration, commercially available, consisting of the following (see Figure 1).

6.2 Tube resistance furnace and combustion tube, capable of maintaining a temperature of (1 150 ± 10) °C in the combustion zone which is at least 70 mm long, with the Pt-Rh-Pt thermocouple and the temperature controller. The combustion tube is made of silicon or corundum, capable of withstanding temperatures greater than 1 300 °C.

6.3 Electrolytic cell and magnetic stirrer.

The electrolytic cell consists of a cylindrical glass cup of over 400 ml capacity, with (120 to 180) mm high, in which there are a pair of Pt electrolytic electrodes each of 150 mm^2 area and a pair of Pt indicating electrodes each of 15 mm^2 area. The response time of indicating electrodes should be less than 1 s. The magnetic stirrer with speed of 500 r/min and regulator is also provided.

6.4 Coulomb integrator.

The integration linearity error is less than 0,1 % at (0 to 350) mA of electrolyzing current, with a (4 to 6 digit) digital display or printer to give the mass fraction of the sulfur in the sample.

6.5 Program controller.

The sample can be pushed into and withdrawn from the combustion tube according to the specified program.

6.6 Purified air stream supply system, consisting of magnetic pumps and purifying tubes and a flowmeter.

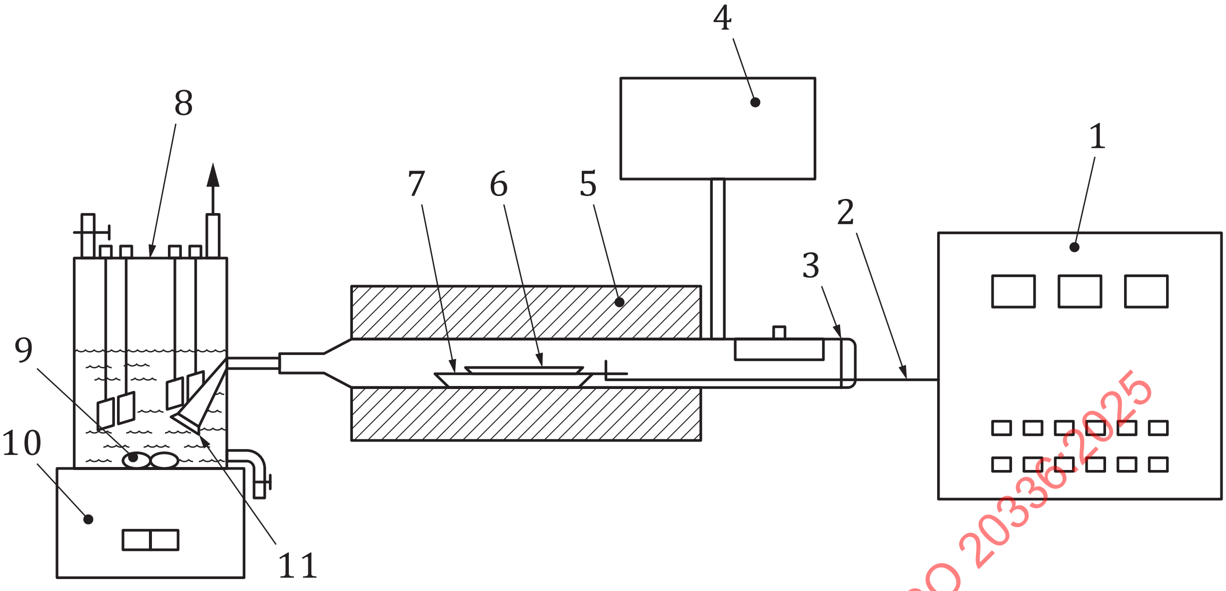
Supply an air stream at the rate of 1 500 ml/min and aspirating it at 1 000 ml/min (indicating by a flowmeter), which is purified and dried by the sodium hydroxide and self-indicating silica gel packed in the purifying tubes respectively (see Figure 2).

NOTE The sodium hydroxide is not necessary for the laboratories in which the air is not polluted by acid gas.

6.7 Combustion boat, made of unglazed porcelain or quartz, about 60 mm long at the part of packing the sample, capable of withstanding over 1 200 °C.

6.8 Quartz tray, capable of withstanding over 1 200 °C and supporting the combustion boat moving in and out the combustion tube.

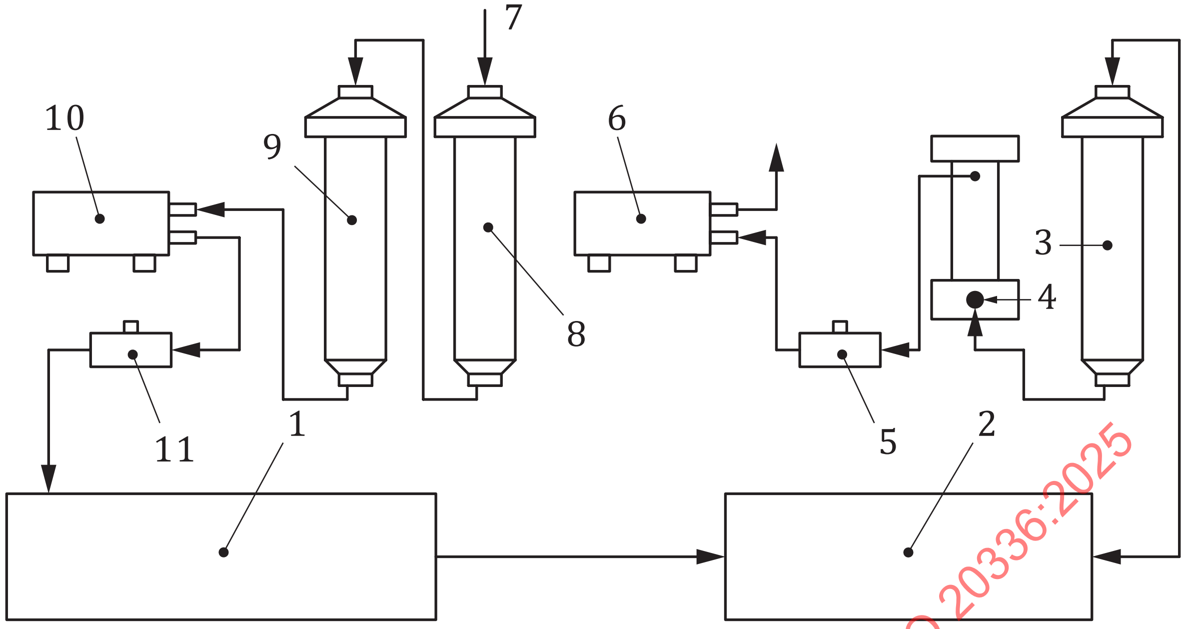
6.9 Analytical balance, having a resolution of 0,1 mg.



Key

1	program controller
2	pulling stem
3	combustion tube
4	purified device for air stream
5	resistance furnace
6	sample boat
7	quartz tray
8	electrolytic cell
9	stirrer stem
10	magnetic stirrer
11	gas filter

Figure 1 — Equipment for determining sulfur by Coulomb titration



Key

1	tube resistance furnace and combustion tube
2	electrolytic cell
3	silica gel
4	flow meter, 1 000 mL/min
5	regulator
6	pump
7	air
8	silica gel
9	NaOH
10	pump
11	regulator

Figure 2 — Purified air stream supply system

7 Preparation of test sample

The coal or coke used for the determination of total sulfur is the general analysis test sample ground to pass a sieve of 212 µm aperture, and for the coal or coke with sulfur higher than 5 % of the sulfur, the general analysis test sample is ground to pass a sieve of 100 µm aperture.

Expose the sample in a thin layer for the minimum time required for the moisture mass fraction to reach to approximate equilibrium with the laboratory atmosphere. Before commencing the determination, thoroughly mix the air-dried sample.

If the results are to be calculated other than on an "air-dried basis", then, after determining the test portion mass (see 8.4.4), the moisture mass fraction shall be determined using a further portion of the test sample by the method specified in ISO 687, ISO 5068-2 or ISO 11722.

8 Procedure

8.1 Preparation of test

8.1.1 Raise the temperature of the furnace to 1 150 °C. Measure the position and length of high temperature zone of (1 150 ± 10) °C and the position of preliminary decomposition zone of 500 °C in combustion tube using a calibrated pyrometer with Pt-Rh-Pt thermocouple.

8.1.2 Adjust the program controller to ensure the combustion boat moves into the position of the preliminary decomposition zone of 500 °C and then to the combustion zone of 1 150 °C automatically.

8.1.3 Fill the clean and dry glass wool (5.7) in the exit end of the combustion tube. Fill the (3 to 5) mm thickness of aluminosilicate wool (5.8) in the area of (80 to 100) mm from the exit end of the combustion tube.

8.1.4 Assemble tube resistance furnace (6.2) with a combustion tube (6.2), electrolytic cell (6.3), magnetic stirrer (6.3), coulomb integrator (6.4), the program controller (6.5), and the purified air stream supply system (6.6). The combustion tube, stopcock and electrolytic cell should be connected in glass to glass closely and sealed with silicone rubber sleeves.

NOTE The assembly and integration processes are usually completed by the manufacturer.

8.1.5 Switch on the pump and adjust aspirating rate of air to 1 000 ml/min, then close the stopcock between the electrolytic cell and the combustion tube. If the aspirating rate of air drops down under 300 ml/min, it indicates that all of parts and joints of the instrument are gas tight. Otherwise, check for the leaks in the system.

8.2 Calibration

Calibrate the instrument according to one of following two methods using the CRMs (5.10) of coal or coke:

a) Multi-point calibration method.

   Calibrate the instrument with at least three CRMs (5.10) of coal or coke that cover the range of sulfur mass fractions that represent the samples.

b) Single-point calibration method.

   Calibration is made with a CRM of coal or coke, in which the sulfur mass fraction is similar to that in the sample.

8.3 Calibration procedure

8.3.1 Determine the moisture of the CRMs of coal or coke (see Clause 7) used as part of the calibration in accordance with drying instructions on the CRM certificate, and by which the air-dried basis of the total sulfur mass fraction of the CRMs are calculated.

8.3.2 Check the instrument to ensure that it is in the normal condition before calibration. Determine the total sulfur mass fraction of the CRMs of coal or coke in accordance with the procedures specified in 8.4. Run a minimum of three times (in triplicate) for every sample. Take the mean value of the replicates as the determined value for sulfur. The replicate results shall agree within the repeatability limit specified in 10.1, if not, check the instrument and repeat the calibration tests.

8.3.3 The calibration factor is calculated from the determined values and the certified values of the CRMs which are calculated to the air-dried basis.

For some instruments, the calibration factors need to be calculated and then put into the instrument manually.