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# Solid mineral fuels — Determination of total sulfur by Coulomb titration method

*Combustibles minéraux solides — Détermination de la teneur totale en soufre par la méthode de titrage de Coulomb*

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# Foreword

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

# Introduction

The objective of this document is to provide an alternative method for determining the total sulfur content in solid mineral fuels with high-temperature combustion — Coulomb titration using automated instruments.

# Solid mineral fuels — Determination of total sulfur by Coulomb titration method

## 1 Scope

This document specifies an alternative method of determining the total sulfur content of coal and coke by high-temperature combustion — 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, *Solid mineral fuels — 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 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 http://www.electropedia.org/

## 4 Principle

In the presence of the catalyst, a weighed sample 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 content 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 content 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.

5 g of potassium iodide (5.1) and 5 g of potassium bromide (5.2) are 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. Combustion tube is made of silicon or corundum, capable of withstanding temperatures greater than 1 300 °C.

### 6.3 Electrolytic cell and magnetic stirrer.

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) digital display or printer to give the content 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.

Consists of the magnetic pumps and purifying tubes. Supply an air stream at the rate of 1 500 ml/min and draw it at 1 000 ml/min, which is purified and dried by the sodium hydroxide and self-indicating silica gel packed in the purifying tubes respectively.

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

### 6.7 Combustion boat.

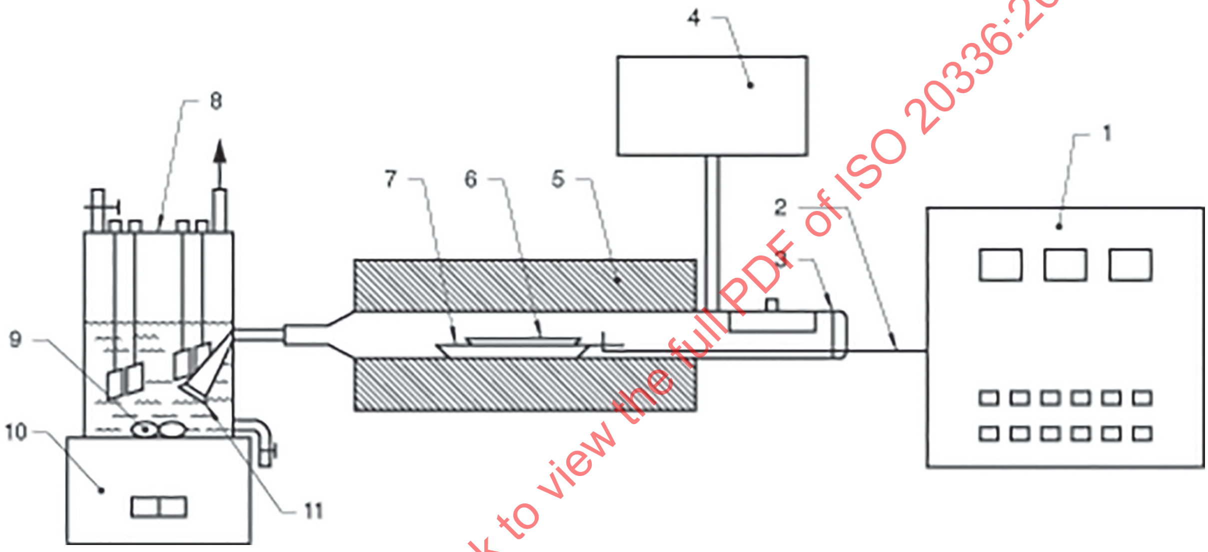
Made of unglazed porcelain or quartz, about 60 mm long at the part of packing the sample, capable of withstanding over 1 200 °C.

### 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.

Capable of weighing to the nearest 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 — Instrument for determining sulfur by Coulomb titration**

## 7 Preparation of test sample

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

Expose the sample in a thin layer for the minimum time required for the moisture content 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 weighing the test portion (see 8.4.4), determine the moisture content 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 so the combustion boat moves into the preliminary decomposition zone of 500 °C and then to the combustion zone of 1 150 °C automatically.

**8.1.3** Pack the exit end of the combustion tube with the clear and dry glass wool (5.7). Pack the place of (80 to 100) mm from the exit end with (3 to 5) mm thickness of aluminosilicate wool (5.8).

**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), purified air stream supply system (6.6). The combustion tube, stopcock and electrolytic cell should be connected in glass to glass closely and seal them with the silicone rubber sleeves.

**8.1.5** Switch on the pump and adjust the rate of suction to 1 000 ml/min, then close the stopcock between the electrolytic cell and the combustion tube. If the rate of suction 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 instrument with at least 3 CRMs (5.10) of coal or coke which cover the range of sulfur contents that represent in the samples.

b) Single-point calibration method

Calibration is made with a CRM of coal or coke, in which the sulfur contents is similar to that represent 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.

**8.3.2** Check the instrument to make sure that it is in the normal condition before calibration. Determine the sulfur content 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.

**8.3.4** Verify the calibration by analyzing another (1 to 2) appropriate CRMs of coal or coke according to the procedures described in 8.4. If the determined result is within acceptable repeatability limits with the CRM, the calibration is valid; otherwise, the reason for the deviation should be investigated, corrected and the instrument recalibrated.

Need to add uncertainty (as a variance) of CRM with repeatability (as a variance). The square root gives the necessary limits. It should be recognized the calibration will be dominated by the CRM with the highest uncertainty.

## 8.4 Procedure

**8.4.1** Raise and maintain the temperature of the furnace to (1 150 ± 10) °C.

**8.4.2** Switch on the magnetic pumps (6.6) of drawing and supplying the air stream. Adjust the rate of the suction to 1 000 ml/min. With the pump operating, add the electrolytic solution (5.6) into the electrolytic cell, then turn on the magnetic stirrer. The electrolytic solution can be reused, but it shall be replaced when pH of the solution is less than 1.

NOTE Check the pH of the electrolytic solution before conducting determinations regularly (after carrying out the experiments of 200 runs or once a week, as a recommendation).

**8.4.3** For adjusting the end-point potential, take about 0.05 g of the previously determined sample into a combustion boat (6.7) and follow the procedure as 8.4.4 and 8.4.5. If the value shown on the Coulomb intergrator is zero after titration, repeat the procedures until it is greater than zero.

**8.4.4** Accurately weigh (0,05 ±0,005) g to nearest 0,000 2 g of the general analysis test sample into the combustion boat and cover the sample with a thin layer of tungsten trioxide(5.9). For the total sulfur content is higher than 5 %, weighing (0,03 ±0,005) g of the ground test sample(see Clause 7) is appropriate. Place the boat on a quartz tray (6.8). Switch on the procedure controller, then the tray is pushed into the combustion tube and stays for a setting time at the preliminary decomposition zone 500 °C and high temperature zone of (1 150 ±10) °C respectively.

NOTE The time of the combustion tray staying in the preliminary decomposition zone is set based on the sample's combustion property and sulfur content, 60 s to 180 s generally.

**8.4.5** Coulomb titration begins once the sample boat enters the combustion tube and terminates when the end-point of the titration is reached. The determined results of sulfur expressed in milligrams or in percentage are shown or printed out.

## 8.5 Calibration check

Calibration check shall be completed periodically after every (10 to 15) runs. The CRMs or other check samples should be analyzed.

If the result is not within repeatability limits of the certified value or known value, the preceding results shall be discarded and the calibration repeated (see 8.2 and 8.3) and the samples reanalysed.