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Solid mineral fuels — Determination of total cadmium content of coal

Combustibles minéraux solides — Dosage du cadmium total dans le charbon

Reference number
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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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 15238:2003), of which it constitutes a minor revision. This document incorporates changes related to dated references and other minor items following its systematic review.

Solid mineral fuels — Determination of total cadmium content of coal

1 Scope

This document specifies a procedure for the determination of the total cadmium content of coal.

This procedure has not been validated with coals that spontaneously ignite. Prior to use with such sample types, users should validate the method.

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 1170, *Coal and coke — Calculation of analyses to different bases*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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*

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

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:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

The coal sample is ashed, followed by dissolution of the ash in a mixture of hydrochloric, nitric and hydrofluoric acids. The cadmium species present are quantified by graphite furnace atomic absorption spectroscopy.

5 Reagents

WARNING — Care should be exercised when handling the reagents, many of which are toxic and corrosive.

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

5.1 Water, conforming to the requirements of Grade 1 of ISO 3696.

5.2 Aqua regia solution. Mix 1 part by volume of concentrated nitric acid solution (relative density 1,42), 3 parts of concentrated hydrochloric acid solution (relative density 1,19), and 1 part water.

5.3 Concentrated hydrofluoric acid solution (relative density 1,15).

WARNING — Hydrofluoric acid is an extremely aggressive chemical which shall be handled with care.

5.4 Boric acid solution, saturated. Dissolve 60 g of boric acid in 1 l of hot water, cool and allow to stand for 3 d before decanting the clear solution.

5.5 Cadmium standard stock solution, 10 μg/ml. Prepare the stock solution from a high purity metal oxide or salt, having a purity greater than 99,9 %. Dilute to volume with 1 % (*V*/*V*) nitric acid solution.

The cadmium standard stock solution may also be prepared from commercially available certified cadmium solution.

5.6 Cadmium standard solution, 0,1 μg/ml. Dilute 10,0 ml of cadmium standard stock solution (5.5) to 1,0 l with 1 % (*V*/*V*) nitric acid solution.

6 Apparatus

6.1 Balance, capable of weighing to the nearest 0,1 mg.

6.2 Silica or platinum combustion crucible (45 mm × 35 mm × 14 mm).

6.3 Muffle furnace, with a temperature control.

6.4 Plastics bottles, made of high density polyethylene (HDPE) or fluorinated ethylene propylene (FEP), of 125 ml capacity, with screw-cap lids, capable of withstanding 130 °C when sealed and containing liquid.

6.5 Volumetric flasks, made of high density polyethylene (HDPE) or fluorinated ethylene propylene (FEP), of 100 ml capacity.

6.6 Boiling-water bath.

6.7 Graphite-furnace atomic absorption spectrometer, with background correction.

7 Preparation of sample

The test sample is the general analysis test sample prepared in accordance with ISO 5069-2 or ISO 13909-4 as appropriate. Ensure that the moisture content of the sample is in equilibrium with the laboratory atmosphere, exposing it if necessary, in a thin layer for the minimum time required to achieve equilibrium.

Before commencing the determination, mix the equilibrated sample for at least 1 min, preferably by mechanical means.

If the results are to be calculated other than on the “air-dried” basis (see Clause 9), then, after weighing the test portion, determine the moisture content of a further portion of the test sample by the method described in ISO 5068-2 as appropriate.

8 Procedure

8.1 Ashing of coal sample

Weigh, to the nearest 0,1 mg, the amount of sample necessary to obtain a minimum of 0,2 g ash in one or more open 50 ml silica combustion crucibles (6.2). The coal layer in the crucible shall not exceed a thickness of 0,15 g/cm^2. Place the crucibles in a cold muffle furnace (6.3), set to attain (450 ± 10) °C in about 1 h, and maintain at that temperature for a further 2 h. After cooling and weighing, calculate the percentage of ash in the coal. Carefully mix the ash in the crucibles before transferring it to a sample bottle.

NOTE The ashing time of 3 h is a minimum. Ashing overnight (18 h) is allowed.

8.2 Preparation of test solution

Place approximately 0,2 g (± 0,1 mg) of ash in a 125 ml plastics bottle (6.4). Add 3 ml of aqua regia (5.2), 5 ml of concentrated hydrofluoric acid solution (5.3), and tighten the screw cap. Place the bottle on a boiling water bath for 2 h. Remove the bottle and allow it to cool to ambient temperature, cautiously open, then add 50 ml of saturated boric acid solution (5.4). Warm again for approximately 1 h; if a residue remains at this stage, it may be ignored. Remove the bottle from the water bath and cool again to ambient temperature before transferring the solution quantitatively to a 100 ml plastics volumetric flask, and diluting to 100 ml with water.

Care should be exercised when adding the acid mixture to the ash since the 450 °C ashing temperature may not have decomposed all carbonates present in the coal.

If desired, it is permitted to prepare the solutions gravimetrically, adjusting the calculations in the appropriate manner.

NOTE As an alternative method for the dissolution of the prepared ash, microwave dissolution or acid dissolution in a pressurized vessel can be used, if quantitative recovery of cadmium can be demonstrated.

8.3 Preparation of blank solution

Prepare a blank solution by following exactly the dissolution procedure described above (see 8.2) but omitting the coal (ash) sample.

8.4 Graphite-furnace atomic absorption analysis

8.4.1 Calibration

Prepare standards by diluting aliquot portions of the cadmium standard solution (5.6), 3 ml of aqua regia solution (5.2), 5 ml of concentrated hydrofluoric acid solution (5.3) and 50 ml of saturated boric acid solution (5.4) to 100 ml with water.

Standards containing 0,0 µg/l, 1,0 µg/l, 2,5 µg/l and 5,0 µg/l have been found suitable. The standards used should be verified for each instrument.

8.4.2 Measurement of standards

Measure the absorbance of each standard solution using the graphite-furnace atomic absorption spectrometer (6.7). Plot the corresponding absorbance response for each matrix-matched standard against concentration, producing a calibration curve for the instrument. Sample responses are then compared directly with the calibration.

The performance of the instrument shall be verified by the analysis of certified reference materials.

NOTE 1 No additional matrix modifier is used for cadmium determination and the instrument parameters allow for this by using a low char temperature.

NOTE 2 An alternative quantification procedure is the use of standard analyte additions to the final solution.

8.4.3 Measurement of test solution

Repeat the procedure described in 8.4.2 for the test solution (see 8.2). Determine the cadmium concentration in the test solution using the calibration graph (see 8.4.2).

8.4.4 Measurement of blank solution

Repeat the procedure described in 8.4.2 for the blank (see 8.3). Determine the cadmium concentration in the blank solution using the calibration graph (see 8.4.2).

9 Expression of results

9.1 Ash content

Calculate the ash content, ω_A, as a percentage by mass of the coal sample, using Formula (1):

$$\omega_A = \frac{(m_c - m_a)}{(m_b - m_a)} \times 100 \quad (1)$$

where

m_a is the mass of the ashing combustion crucible;

m_b is the mass of the ashing combustion crucible plus coal before ashing;

m_c is the mass of the ashing combustion crucible plus coal after ashing.

9.2 Cadmium content

Calculate the cadmium content, ω_{Cd}, in ng/g, in the coal test sample using Formula (2):

$$\omega_{Cd} = \omega_A \frac{(\rho_t - \rho_b)}{1\,000\,m} \times 1\,000 \quad (2)$$

where

ω_A is the ash content of the sample as analysed, in percentage by mass;

ρ_t is the cadmium concentration of the test solution, in µg/l;

ρ_b is the cadmium concentration of the blank solution, in µg/l;

m is the mass of the sample as analysed, in grams.

Report the result as the mean of duplicate determinations to the nearest 20 ng/g on the "as analysed" basis.

For calculation of the results to bases other than "as analysed", see ISO 1170.

10 Precision

10.1 Repeatability limit

The means of the results of duplicate determinations, carried out at different times, in the same laboratory, by the same operator, with the same apparatus, on representative portions taken from the same general analysis sample, should not differ by more than the value given in Table 1.

10.2 Reproducibility critical difference

The results of duplicate determinations, carried out in each of two laboratories, on representative portions taken from the same analysis sample after the last stage of sample preparation, should not differ by more than the value given in Table 1.

Table 1

	Maximum acceptable differences between results obtained (calculated to the same moisture content)	
	Repeatability limit	**Reproducibility critical difference**
Cadmium content (ng/g)	$0{,}16\omega_{\mathrm{Cd}} - 1$	$0{,}22\omega_{\mathrm{Cd}} + 3$

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 15238;

c) the date of the determination;

d) the results and the method of expression used.

ICS 73.040

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