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Solid mineral fuels — Determination of total mercury content of coal

National foreword

This British Standard is the UK implementation of ISO 15237:2016. It supersedes BS ISO 15237:2003 which is withdrawn.

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Solid mineral fuels — Determination of total mercury content of coal

Combustibles minéraux solides — Dosage du mercure total dans le charbon

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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 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 15237:2003), which has been technically revised. This document incorporates changes related to dated references and other minor items following its systematic review.

Introduction

Mercury occurs naturally in coal. It is an element that can be released during the combustion process.

The determination of the total mercury content of coal cannot be accomplished satisfactorily by traditional ashing and digestion procedures because of the volatility of the element.

Quantitive recovery can be achieved by strict adherence to the procedure set out in this document.

Instrumental methods for a more rapid determination of total mercury content are available. If such a method is to be used, it is important to demonstrate that the method is free from bias, when compared with this reference method and will give levels of repeatability and reproducibility which are the same, or better than, those quoted for the reference method (see Clause 10).

Solid mineral fuels — Determination of total mercury content of coal

1 Scope

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

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 1928, *Solid mineral fuels — Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value*

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 definition

No terms and definitions are defined 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 sample is burned in an oxygen bomb, the mercury species formed during combustion being absorbed in water. The mercury species present in the water are reduced by stannous chloride and quantified by flameless cold vapour atomic absorption spectroscopy.

It is reported that lithium borohydride ($LiBH_4$) and sodium borohydride ($NaBH_4$) are satisfactory for the reduction instead of stannous chloride; laboratories using these reductants should demonstrate that the performance is equivalent to that using stannous chloride.

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 Grade 1 of ISO 3696.

5.2 Oxygen, free from combustible matter and having a purity of at least 99,5 %.

5.3 Nitric acid solution, 10 % by volume, prepared by diluting 100 ml of concentrated nitric acid (relative density 1,42) to 1 litre with water. The 10 % solution shall have a mercury content less than 0,1 µg/l.

5.4 Mercury standard stock solution, 1 000 µg/ml, prepared by dissolving 1,0 g of high purity mercury in 5 ml of 25 % (*V*/*V*) nitric acid solution and diluting to 1 000 ml.

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

Other high purity (>99,9 %) mercury salts or oxides may be used with appropriate adjustment of the mass taken.

5.5 Mercury standard solution, 0,1 µg/ml, prepared by diluting 5,0 ml of mercury standard stock solution (5.4) to 500 ml with water and then diluting 10,0 ml of the intermediate solution to 1 litre with water.

This mercury standard solution should be prepared daily.

5.6 Potassium permanganate solution, 50 g/l, prepared by dissolving 5 g of potassium permanganate ($KMnO_4$) in water and diluting to 100 ml.

The mercury content of the potassium permanganate should be below 0,05 µg/g.

5.7 Hydroxylammonium chloride solution, 15 g/l, prepared by dissolving 1,5 g of hydroxylammonium chloride ($HONH_3Cl$) in water and diluting to 100 ml.

The mercury content of the hydroxylammonium chloride should be below 0,005 µg/g.

5.8 Reducing agent, stannous chloride solution, 100 g/l, prepared by dissolving 10 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 45 ml of concentrated hydrochloric acid solution (relative density 1,19) and cautiously diluting to 100 ml with water.

The mercury content of the stannous chloride dihydrate should be below 0,01 µg/g.

NOTE See also Note 1 to 10.2 regarding the use of flow injection techniques.

6 Apparatus

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

6.2 Oxygen combustion bomb, constructed in accordance with ISO 1928. The ignition wire shall be platinum or chromium-nickel alloy. The combustion bomb shall be constructed of materials that are not affected by the combustion process or products. In particular, the combustion bomb shall be constructed of material that is free from mercury. This can be verified by washing the interior surfaces with dilute nitric acid (50 ml, 10 % *V*/*V*), and determining the mercury content of the washings. This shall be <0,01 µg per bomb. The combustion bomb shall also be designed so that all liquid combustion products can be completely recovered.

WARNING — The combustion bomb should be inspected regularly for signs of corrosion caused by the strong acid used in the procedure.

6.3 Silica combustion crucible, to fit oxygen combustion bomb.

6.4 Atomic absorption spectrometer, with a flameless cold-vapour mercury analysis system, comprised of either a closed recirculating system or an open one-pass system.

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 11), 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 Oxygen bomb combustion procedure

8.1 General

Clean all internal components of the combustion bomb (the body, cap and electrodes) by immersion in 10 % nitric acid solution for 5 min followed by thorough washing with water before use. Using paper towels, dry the threads on the combustion bomb body and locking ring. Repeat the washing step between each determination.

8.2 Combustion of coal

Weigh approximately 1 g of test portion, to the nearest 0,1 mg, into a pre-ignited crucible.

Assemble the ignition system using ignition wire and ignition thread.

Pipette 10 ml of water into the base of the combustion bomb and assemble.

Charge the bomb with oxygen (5.2) to 3 MPa pressure.

Place the assembled combustion bomb in the calorimeter can containing 2 litres of water and fire using the ignition/firing station. Allow the combustion bomb to stand in the calorimeter can for 10 min before removal.

Dry external surfaces of the bomb thoroughly with paper towel, keeping the bomb upright, before carefully venting the bomb gases over a period of 2 min.

9 Preparation of test solution

Disassemble the combustion bomb and carefully rinse all internal surfaces, including the crucible, with water, collecting all washings in the bomb.

Using a disposable syringe, transfer the bomb washings to a 100 ml volumetric flask containing 10 ml of 10 % nitric acid solution (5.3). Wash the bomb with water, adding the washings to the volumetric flask. Add 0,5 ml of potassium permanganate solution (5.6) and mix. Dilute to volume with water.

Carry out a blank determination following exactly the procedure described above but omitting the coal sample.

In those cases where the design of the bomb precludes a 1 g test portion being used, a suitable smaller quantity should be taken.

NOTE The transfer of the bomb washings by syringe is important since it has been shown that the bomb locking ring in some calorimeters is a source of mercury contamination which is transferred to the threads of the body. If the bomb washings are poured out in these cases, significant mercury contamination results due to contact between washings and the threads on the bomb body. For calorimeter types initially shown to give no contamination, the transfer by syringe is not necessary. In every analysis, the documentation for this is achieved by the blank determination.

10 Atomic absorption analysis

10.1 Calibration

Prepare matrix-matched mercury standards of 3,0 µg/l, 5,0 µg/l and 10,0 µg/l by pipetting 3,0 ml, 5,0 ml and 10,0 ml aliquot portions of the 0,1 µg/ml mercury standard solution (5.5) into 100 ml graduated flasks, adding 10 ml of 10 % nitric acid solution (5.3) and diluting to volume with water. Add potassium permanganate solution (5.6) dropwise to stabilize the solutions until the permanganate colour persists for 60 s.

Measure the absorbance for each matrix-matched solution in accordance with 10.2. For instrument calibration, the absorbance for each matrix-matched solution is plotted against the corresponding concentration. Sample responses are compared with this calibration.

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

10.2 Analytical procedure

The calibration solutions prepared in accordance with 10.1, and the test solutions and the blank solutions prepared in accordance with Clause 9 are all treated as follows.

Transfer the prepared solution into a suitable mercury-free vessel and heat at 90 °C for 60 min on a digestion block or water bath. Cool.

Transfer the prepared solution into the reaction vessel, add 5 ml of hydroxylammonium chloride solution (5.7) to the solution. When the permanganate colour fades, wait 30 s and add 5 ml of the reducing agent, stannous chloride solution (5.8).

Exact details for use of the instrumentation cannot be given as each instrument is different. Depending on the instrumentation being used, it may be necessary to use the complete 100 ml prepared sample or an aliquot of the prepared sample. Whichever approach is used, samples, standards and blanks shall be treated in an identical manner.

Immediately connect the flask to the flameless cold-vapour atomic absorption spectrometer (6.4) to complete the mercury determination.

The corresponding absorbance response for each test and blank solution is compared with the calibration curve (see 10.1) and the resultant concentration, in µg/l, is noted.

NOTE 1 The mercury reduction stage can be improved by the use of a flow injection technique in which the reagents are fed automatically to the instrument. Experience has shown that, when using stannous chloride, a solution of 1 % (*m*/*V*) stannous chloride dihydrate in 3 % (*V*/*V*) hydrochloric acid is suitable for this technique.

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

11 Expression of results

Calculate the mercury content, ω, expressed in ng/g of the sample as analysed, using Formula (1):

$$\omega = \frac{\left(\rho_\mathrm{t} - \rho_\mathrm{b}\right)}{10\ m} \times 1\ 000 \qquad (1)$$

where

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

ρ_b is the mercury 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.

12 Precision

12.1 Repeatability limit

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.

12.2 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**
Mercury content (ng/g)	$0{,}14\omega + 8$	$0{,}25\omega + 20$

13 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;

c) the date of the determination;

d) the results and the method of expression used.

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