INTERNATIONAL
STANDARD

**ISO
11723**

Second edition
2016-11-15

Solid mineral fuels — Determination of arsenic and selenium — Eschka's mixture and hydride generation method

Combustibles minéraux solides — Dosage de l'arsenic et du sélénium — Mélange d'Eschka et méthode par production d'hydrure

Reference number
ISO 11723:2016(E)

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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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 minerals fuels*, Subcommittee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 11723:2004), which has been technically revised. This document incorporates changes related to dated references and other minor items following its systematic review.

Solid mineral fuels — Determination of arsenic and selenium — Eschka's mixture and hydride generation method

1 Scope

This document specifies a method using Eschka's mixture during ashing, extraction of the ash residue with acid, and hydride generation atomic absorption spectrometry or hydride generation atomic fluorescence spectrometry, for the determination of arsenic and selenium in solid mineral fuels.

NOTE The method is also applicable to the determination of the analytes by hydride generation inductively coupled plasma atomic emission spectrometry.

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

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

ISO 13909-6, *Hard coal and coke — Mechanical sampling — Part 6: Coke — 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

A known mass of the sample is ignited in intimate contact with Eschka's mixture in an oxidizing atmosphere at 800 °C to remove the organic matter. The residue is then extracted with hydrochloric acid and the analytes determined by hydride generation atomic absorption spectrometry or hydride generation atomic fluorescence spectrometry.

5 Reagents

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

During the analysis, unless otherwise stated, use only reagents of recognized analytical reagent grade and water conforming to Grade 1 of ISO 3696.

5.1 Eschka's mixture, composed of two parts by mass of light magnesium oxide and one part by mass of anhydrous sodium carbonate.

5.2 Hydrochloric acid (ρ_{20} 1,19 g/ml).

5.3 Nitric acid (ρ_{20} 1,42 g/ml).

5.4 Potassium iodide solution, 500 g/l. Dissolve 50 g of analytical reagent (AR) grade KI in distilled water and adjust the volume to 100 ml (for determination of As).

5.5 Sodium borohydride solution. Weigh 1,50 g of sodium borohydride ($NaBH_4$) and 0,4 g of sodium hydroxide (NaOH) into a plastic bottle of 125 ml capacity and add 100 ml of distilled water. Prepare freshly on the day of use. Alternatively, commercially available pressed pellets of sodium borohydride may be used.

5.6 Arsenic stock solution (100 mg/l). Dissolve 0,132 0 g ± 0,000 5 g of arsenic trioxide (As_2O_3 of 99,9 % purity, dried at 110 °C for 1 h) in 25 ml of 20 % KOH solution. Add approximately 50 ml of water and 20 ml of hydrochloric acid (5.2). Adjust the volume with water to 1 litre in a volumetric flask. Alternatively, dissolve 0,416 5 g ± 0,000 5 g of sodium arsenate ($Na_2HAsO_4.7H_2O$) in approximately 100 ml of water. Add 10 ml of hydrochloric acid (5.2) and adjust the volume with water to 1 l in a volumetric flask.

NOTE A commercially available certified stock solution may be used as an alternative.

5.7 Dilute arsenic stock solution (1 mg/l). Transfer 5 ml of arsenic stock solution to a 500 ml volumetric flask. Add approximately 100 ml of water and 5 ml of hydrochloric acid (5.2). Adjust to volume with water.

5.8 Arsenic working standard (50 µg/l). Transfer 5 ml of dilute arsenic stock solution (5.7) to a 100 ml volumetric flask. Add approximately 20 ml of water and of 1 ml hydrochloric acid (5.2). Adjust to volume with water. Prepare freshly on the day of measurement.

5.9 Selenium stock solution (100 mg/l). Dissolve 0,100 0 ± 0,000 5 g of elemental selenium (of 99,9 % purity) in a minimum of nitric acid in a beaker. Evaporate to dryness. Add 2 ml of water and evaporate to dryness; repeat this procedure twice. Add 10 ml of water to the residue and 10 ml of hydrochloric acid (5.2). Dissolve the residue by heating. Allow the solution to cool and adjust the volume with water to 1 l in a volumetric flask. Alternatively, dissolve 0,467 4 g ± 0,000 5 g of sodium selenate ($Na_2SeO_4.10H_2O$) in approximately 100 ml of water. Add 10 ml of hydrochloric acid (5.2) and adjust the volume with water to 1 l in a volumetric flask.

NOTE A commercially available certified stock solution may be used as an alternative.

5.10 Dilute selenium stock solution (1 mg/l). Transfer 5 ml of selenium stock solution (5.9) to a 500 ml volumetric flask. Add approximately 100 ml of water and 5 ml of hydrochloric acid (5.2). Adjust to volume with water.

5.11 Selenium working standard (50 µg/l). Transfer 5 ml of dilute selenium stock solution (5.10) to a 100 ml volumetric flask. Add approximately 20 ml of water and 1 ml of hydrochloric acid (5.2). Adjust to volume with water. Prepare freshly on the day of measurement.

6 Apparatus

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

6.2 Crucible, a shallow silica crucible of capacity approximately 25 ml.

6.3 Silica plate, 6 mm thick, having an easy sliding fit in the muffle furnace.

6.4 Muffle furnace, capable of obtaining 800 °C over 2 h from ambient temperature.

6.5 Plastic bottle, wide necked, of capacity 60 ml (autoclavable) with screw-threaded lid.

6.6 Atomic absorption spectrometer or **atomic fluorescence spectrometer**, equipped with a hydride generation apparatus.

To minimize potential contamination, clean all laboratory ware with dilute HCl (1 + 10).

7 Preparation of the test sample

The test sample is the general analysis sample, prepared in accordance with ISO 5069-2, ISO 13909-4 or ISO 13909-6, as appropriate. Expose the sample in a thin layer for the minimum time required for the moisture content to reach approximate equilibrium with the laboratory atmosphere.

Before commencing the determination, mix the equilibrated sample thoroughly.

If the results are to be calculated to other than on an 'as analysed' basis i.e. air-dried (see Clause 10), concurrently determine the moisture content using a further portion of the test sample by the method described in ISO 5068, ISO 11722 or ISO 687, as appropriate.

8 Procedure

8.1 Blank determination

A blank determination shall be carried out at the same time and under the same conditions as the actual determination, but omitting the sample.

8.2 Preparation of test solution

The procedure, carried out in duplicate, shall be as follows.

Weigh, to the nearest 0,000 1 g, a test portion of approximately 0,5 g and mix intimately with 0,8 g of Eschka's mixture (5.1) in the crucible (6.2). Level the contents of the crucible and cover with 0,2 g of Eschka's mixture.

Place the charged crucible on the cold silica plate (6.3). Insert both into the cold muffle furnace (6.4) and heat at a uniform rate to 800 °C for 2 h. Maintain at this temperature for a further 2 h.

Remove the silica plate and crucible from the furnace and allow to cool.

Transfer the contents of the crucible to the tared plastic bottle (6.5). Wash the residue into the bottle with 5 ml to 10 ml of water (alternatively into a 100 ml beaker).

Add 10 ml of hydrochloric acid (5.2) to the crucible and gently warm on a hotplate. Transfer to the bottle (or beaker). Wash the crucible with a further 5 ml of water and transfer the washings to the bottle (alternatively to a beaker). Shake gently to allow the evolution of any carbon dioxide produced.

WARNING — Hydrochloric acid must be added carefully as the reaction with Eschka's mixture is exothermic and releases carbon dioxide.

Allow the bottle to cool and adjust the mass of solution to 50,0 g with water (alternatively, transfer the solution from the beaker to a 50 ml volumetric flask and make up to volume).

8.3 Preparation of calibration standards

Add 1 g of Eschka's mixture (5.1) to four tared plastic bottles (6.5) (alternatively to beakers). Add approximately 10 ml of water and 20 ml of hydrochloric acid (5.2) to dissolve the Eschka's mixture.

Allow the solutions to cool. Adjust one solution to 50,0 g (alternatively, transfer solution to 50 ml volumetric flasks and adjust one to volume with water). This is the calibration blank. To the other bottles (or flasks), add respectively, 1,00 ml, 2,00 ml and 3,00 ml ± 0,02 ml of the appropriate working standard (5.8) or (5.11). Adjust the mass of solution to 50,0 g (alternatively 50,0 ml). These calibration standards are 1 µg/kg, 2 µg/kg and 3 µg/kg of solution (or µg/l).

8.4 Preparation for measurement

8.4.1 General

Solutions are prepared as in 8.4.2 and 8.4.3.

8.4.2 Arsenic

Pipette 10 ml of each calibration standard and test solution, including blanks, of solution into separate plastic vials of capacity approximately 30 ml.

Add 5 ml of hydrochloric acid (5.2) to each vial.

Add 0,5 ml of potassium iodide solution (5.4) to each vial and let stand for 20 min.

8.4.3 Selenium

Pipette 10 ml of each calibration standard and test solution, including blanks, into tall beakers or test tubes of capacity 25 ml to 50 ml. Add 5 ml of HCl. Heat at 90 °C for 15 min to 20 min to reduce selenite to selenium.

Do not boil or heat solutions in beakers or test tubes for longer than 20 min as selenite can be reduced to elemental selenium. The effectiveness of the reduction process can be assessed by "reducing" a calibration standard of sodium selenate and comparing the result with an unreduced standard prepared from sodium selenite

Cool the solutions and adjust the volume to the original value, 15 ml.

9 Measurement by atomic absorption or atomic fluorescence spectrometry after hydride generation

The spectrometer and hydride generation apparatus are optimized according to the manufacturer's advice. Arsenic is measured at 193,7 nm and selenium at 196,0 nm.

NOTE 1 It is not possible to specify instrumental operating conditions because the instruments available vary significantly and incorporate alternative methods of hydride generation and atomization.

NOTE 2 As an alternative to the use of an atomic absorption spectrometer or an atomic fluorescence spectrometer, an inductively coupled plasma atomic emission spectrometer equipped with hydride generation apparatus can be used.

Transfer the prepared solution (8.4) into the hydride generation apparatus, add the appropriate amount of sodium borohydride solution (5.5) or a pellet of sodium borohydride and transport the generated hydride of the analyte into the atomization device in the light path of the spectrometer. Note the absorbance or fluorescence signal (peak height or peak area).

Repeat the measurement procedure for all blanks, calibration standard solutions and test solutions.

If the reading for any test solution is higher than that of the highest calibration standard solution, then the test solution shall be diluted with the blank test solution and remeasured, at the same time noting the dilution factor.

From the readings obtained on the calibration standard solutions, construct a calibration graph of concentration of analyte, in µg/kg or µg/l, versus instrument reading (peak height or peak area). The concentration of arsenic or selenium in the sample test solution is obtained from the graph.

Using the prepared calibration graph, convert the readings obtained on the test and blank test solutions to concentrations in µg/kg of test solution or µg/l.

10 Expression of results

The concentration of As and Se in the sample, expressed as µg/g, is given by the following formulae:

$$\text{As in sample} = \frac{C_{\text{As}} - B_{\text{As}}}{10^3} \times \frac{50}{m} \times \frac{F}{1} \tag{1}$$

$$\text{Se in sample} = \frac{C_{\text{Se}} - B_{\text{Se}}}{10^3} \times \frac{50}{m} \times \frac{F}{1} \tag{2}$$

where

C_{As} is the concentration of As in the test solution, in or µg/kg or µg/l;

B_{As} is the concentration of As in the blank test solution, in or µg/kg or µg/l;

C_{Se} is the concentration of Se in the test solution, in or µg/kg or µg/l;

B_{Se} is the concentration of Se in the blank test solution, in or µg/kg or µg/l;

m is the mass of sample, in g;

F is the dilution factor, if applicable.

Report the results as the mean of duplicate determinations to the nearest 0,1 µg/g on the “as analysed” basis, together with the moisture content of the “as analysed” sample.

Calculate the results to bases other than “as analysed”, i.e. air-dried in accordance with ISO 1170.

11 Precision

11.1 Repeatability

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

Table 1 — Precision data for arsenic and selenium

Concentration μg/g	Repeatability	Reproducibility
< 1	0,1 μg/g	0,2 μg/g
≥ 1	10 % relative	20 % relative

11.2 Reproducibility critical difference

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

12 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 11723;

c) the date of the determination;

d) the results and the method of expression used.

ICS 73.040

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