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Coal — Selection of methods for the determination of trace elements — Guidance and requirements

Charbon — Sélection des méthodes de détermination des éléments traces — Recommandations et exigences

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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 of the voluntary nature of standards, 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 www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 23380:2013) which has been technically revised.

The main changes are as follows:

— The title has been changed to add "Guidance and requirements";

— Clause 9, Reporting of results including Table 2, Clause 10, Precision and Clause 11, Test Report, have been removed.

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 determination of trace elements in coal and coke is becoming more important due to the considerable emphasis being placed on the effect of these elements on the environment. In order to have accurate and precise results for the analysis of trace elements, it is imperative that standard methods be available and that these methods be based on reliable procedures.

The objective of this document is to assist in the selection of the appropriate methods available to determine the common trace elements in coal.

Coal — Selection of methods for the determination of trace elements — Guidance and requirements

1 Scope

This document provides guidance and requirements on the selection of methods used for the determination of trace elements in coal. The trace elements of environmental interest include antimony, arsenic, beryllium, boron, cadmium, chlorine, chromium, cobalt, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, thallium, vanadium and zinc. The radioactive trace elements thorium and uranium can be added to this list.

This document does not prescribe the methods used for the determination of individual trace elements. The analysis of appropriate certified reference materials (CRMs) is essential to confirm the accuracy of any method used (see ISO Guide 33).

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 1213-2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement methods and results*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1213-2 apply.

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 Abbreviated terms

AAS	atomic absorption spectrometry
AFS	atomic fluorescence spectrometry
CRM	certified reference material
GFAAS	graphite-furnace atomic absorption spectrometry
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectrometry — often referred to as ICP-OES, i.e. inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ISE	ion-selective electrode
XRF	X-ray fluorescence spectrometry

5 Discussion of methods

5.1 General

A summary of techniques applicable to the determination of each of the trace elements is discussed below. A schematic of procedures used for trace element determinations is given in Annex A.

Moisture shall be determined on the sample to enable calculation to bases other than "air-dried". Moisture determination is described in ISO 11722.

NOTE 1 There are digestion procedures applicable to unashed coal given in Annex B.

NOTE 2 Boron, chlorine, fluorine, mercury, and selenium are released if coal is ashed; thus, it is not possible to estimate the mass fraction of these elements in coal by analysing laboratory-prepared ash.

Where digestion procedures require ashing of the coal, ash yield shall be determined to enable calculation of trace element mass fractions in the coal sample (see Clause 7). Ashing procedures are described in ISO 15238. Coals are ashed in silica or quartz dishes, or in platinum or platinum alloy crucibles/basins, in a conventional ashing furnace. The furnace temperature is ramped from ambient to a maximum of 500 °C over 1 h to 3 h and held at this temperature until the carbonaceous material is completely oxidized or for a maximum of 18 h. The ramp rate is selected to avoid ignition and mechanical loss of sample.

5.2 Arsenic and selenium

Arsenic and selenium are determined by hydride generation/atomic absorption or atomic fluorescence techniques following the ashing of the coal at 800 °C in the presence of Eschka mixture and dissolution with hydrochloric acid. ISO 11723 is the recommended method for the determination of arsenic and selenium in coal.

Arsenic can be determined in coal by the analysis of ash prepared in a laboratory at a temperature no greater than 500 °C. Selenium is vaporized at quite low temperatures and is not recovered in ash. There is no International Standard for the determination of arsenic in coal ash. A suitable procedure is the dissolution of the ash either by fusion (lithium tetraborate/metaborate) or by mixed acids (nitric, hydrochloric, and hydrofluoric acids) and determination of the analyte by hydride/AAS or hydride/AFS. This element can also be determined by ICP-MS if the interference caused by argon chloride is eliminated.

5.3 Boron

Boron is determined by ICP-AES following the ashing of the coal at 800 °C in the presence of Eschka mixture and dissolution with hydrochloric acid (see AS 1038.10.3). This dissolution procedure is the same as that used for arsenic and selenium. The procedure is set out in ISO 11723.

5.4 Antimony, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, thallium, vanadium, zinc, thorium and uranium

5.4.1 General

Antimony, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, thallium, vanadium, zinc, thorium, and uranium are determined by various spectrometric techniques (see ASTM D6357). ASTM D6357 pertains to the determination of antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, vanadium, and zinc in coal and coke. The determination of rare earth elements, cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, samarium, scandium, terbium, thulium, ytterbium, and yttrium are also within the scope of this standard.

NOTE 1 A number of these trace elements can be determined by XRF. However, in general, the sensitivity is too low to accurately determine beryllium, cadmium, thallium, thorium, and uranium by XRF.

Recommended procedures are summarized below.

a) The coal sample is ashed at a maximum temperature of 500 °C to remove the carbonaceous matter.

b) The laboratory-prepared ash is dissolved either by lithium tetraborate/metaborate fusion (see AS 1038.14.1) or by mixed acids (nitric, hydrochloric, and hydrofluoric acids). These dissolution procedures are applicable to the analysis of coal ash. Thorium and uranium can form insoluble fluorides and precautions shall be taken to prevent the formation of these insoluble fluorides in the presence of hydrofluoric acid. Thorium and uranium can be determined within 2 h of the preparation of a mixed-acid solution of the coal ash or the fluoride can be removed by evaporation.

The solution obtained by dissolution procedures in which fluoride is complexed with boric acid can be used for the determination of trace elements by ICP-AES and ICP-MS.

c) The mass concentration of the analytes in the solution are determined by spectrometric techniques. Traditionally, AAS has been used. This has generally been replaced by ICP-AES, which is used to determine the majority of these elements with the exception of antimony, cadmium, lead, thallium, thorium and uranium. These latter six elements occur in coals at mass fractions too low to be determined by ICP-AES but can be accurately determined by ICP-MS.

NOTE 2 Cadmium (see ISO 15238) and lead can also be determined by GFAAS.

5.4.2 Radionuclides

Radionuclides are naturally present in coal. Their radioactivity can be measured using high-resolution gamma spectrometry[15]. This radioactivity is due to the decay of ^{238}U, ^{235}U, and ^{232}Th and their daughters, as well as ^{40}K and ^{87}Rb.

5.5 Chlorine

Chlorine can be determined by a number of methods, including ISO 587, ISO 18806 and ASTM D4208. These procedures require that the coal be burnt and the chlorine trapped either in Eschka mixture or in an alkaline solution. The methods lack sensitivity and, with these procedures, repeatability levels are high. The solution obtained by pyrohydrolysis (see 5.6) can be used for the measurement of chlorine by IC or ICP-AES. The use of XRF according to ISO 13605 can provide a practical and accurate method for the determination of chlorine directly on the coal.

NOTE Chlorine is generally reported not as a trace element but as a minor element and expressed as a percentage.

5.6 Fluorine

Fluorine is determined using ISO 11724. This method is a pyrohydrolysis/ISE or pyrohydrolysis/IC procedure. This procedure can be used for the analysis of coal ash. There is significant evidence in the scientific literature that methods based on the decomposition of coal with an oxygen bomb combustion procedure can give low results.

NOTE Fluorine and chlorine can also be reported together, in which case fluorine is not reported as a trace element.

5.7 Mercury

Mercury is determined using ISO 15237. In this procedure, coal is combusted in an oxygen bomb and the released mercury absorbed in a solution of dilute nitric acid. A number of accurate alternative procedures exist for the determination of mercury. It is possible to digest coal with acids, either in a pressure vessel in a microwave oven or closed vessel in a heated water bath, or by refluxing with a mixture of nitric and sulfuric acids (see ASTM D6414). There are instrumental techniques in which the coal is combusted and the released mercury adsorbed onto a gold collector. The mercury is subsequently thermally released and concentrated (see ASTM D6722).

6 Use of certified reference materials

The use of appropriate CRMs is absolutely essential when checking the accuracy of methods for the determination of trace elements in coal (see ISO Guide 33). CRMs of coal are available and are required to ascertain that there are no losses of analytes during the ashing procedure of any method. CRMs of coal ash can be used for those methods that require the ashing of the coal as a part of the procedure.

The verification of the method selected to determine trace elements shall be confirmed by using the procedures in ISO 5725 (all parts) and documented.

A CRM should be analysed with each batch of samples and the result of this analysis should be reported on the test report, together with the certified or recommended values.

7 Calculation of results

The mass fraction of element *X*, $w_{\mathrm{X,coal\ dry}}$, expressed in milligrams per kilogram of coal on a dry basis, where the analyte has been determined without ashing of the sample, is calculated using Formula (1):

$$w_{\mathrm{X,d\ coal}} = w_{\mathrm{X,ad\ coal}} \times \frac{100}{100 - M_{\mathrm{ad}}} \tag{1}$$

where

M_{ad} is the moisture in coal, air-dried basis, as a percentage;

$w_{\mathrm{X,ad\ coal}}$ is the mass fraction of element *X* in coal, in milligrams per kilogram, air-dried basis;

100 is the conversion factor from dimensionless mass fraction to per cent, %.

The calculation of $w_{\mathrm{X,coal\ ad}}$ to an air-dried coal basis where the sample was ashed prior to the determination of the analyte is given by Formula (2):

$$w_{\mathrm{X,ad\ coal}} = w_{\mathrm{X,ash}} \times \frac{w_{\mathrm{A500}}}{100} \tag{2}$$

where

$w_{\mathrm{X,ash}}$ is the mass fraction of element *X*, expressed in milligrams per kilogram of ash;

w_{A500} is the ash yield (mass fraction) of general analysis test sample at 500 °C, in %.

8 Sensitivity

All methods used for the determination of trace elements in coal shall have adequate sensitivity to detect the levels present in coal. Typical mass fraction ranges of the trace elements in traded coals are listed in Table 1. The detection limits and precision required of methods are also listed.