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Selection of methods for the determination of trace elements in coal

Sélection des méthodes de détermination des éléments en traces dans le charbon

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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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 23380:2008), of which it constitutes a minor revision.

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 International Standard is to assist in the selection of the appropriate methods available to determine the common trace elements in coal.

Selection of methods for the determination of trace elements in coal

1 Scope

This International Standard provides guidance 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 International Standard 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, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

ISO Guide 33, *Reference Materials — Good practice in using reference materials*

3 Terms and definitions

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

4 Abbreviations

AAS	atomic absorption spectrometry
AFS	atomic fluorescence spectrometry
CVAAS	cold-vapour atomic absorption spectrometry
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
INAA	instrumental neutron activation analysis
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.

It is critical that moisture be determined on the sample to enable calculation to bases other than "air-dried".

NOTE 1 There are digestion procedures applicable to unashed coal. The application of these is discussed 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 concentration of these elements in coal by analysing laboratory-prepared ash.

Where digestion procedures require ashing of the coal, it is critical to determine the ash yield to enable calculation of trace elements content in the coal sample (see Clause 7). Ashing procedures are described in ISO 15238[6]. 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[3] 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 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[3].

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).

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 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. Note that thorium and uranium can form insoluble fluorides and precautions shall be taken to prevent this 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 concentrations 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 concentrations 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. The radioactivity of these can be measured using high-resolution gamma spectrometry; refer to Fardy, et al.[14]. This radioactivity is due to the decay of 238U, 235U, and 232Th and their daughters, as well as 40K and 87Rb.

5.5 Chlorine

Chlorine can be determined by a number of methods, including ISO 587[1] and ASTM D4208[9]. 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 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[4]. 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.

5.7 Mercury

Mercury is determined using ISO 15237[5]. 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.