BS ISO 23380:2013

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Selection of methods for the determination of trace elements in coal

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The UK participation in its preparation was entrusted to Technical Committee PTI/16, Solid mineral fuels.

A list of organizations represented on this committee can be obtained on request to its secretary.

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INTERNATIONAL STANDARD

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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

Reference number
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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.

INTERNATIONAL STANDARD **ISO 23380:2013(E)**

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.

It is mandatory that verification of the method selected to determine trace elements be confirmed by using the procedures in ISO 5725 (all parts) and that this verification be documented.

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

7 Calculation of results

The concentration of element *X*, $C_{X,\text{coal dry}}$, 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):

$$C_{X,\text{coal dry}} = C_{X,\text{coal ad}} \times \frac{100}{100 - M_{\text{ad}}} \quad (1)$$

where:

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

$C_{X,\text{coal ad}}$ is the concentration of element *X* in coal, in milligrams per kilogram, air-dried basis.

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

$$C_{X,\text{coal ad}} = C_{X,\text{ash}} \times \frac{A_{500}}{100} \quad (2)$$

where:

$C_{X,\text{ash}}$ is the concentration of element *X*, expressed in milligrams per kilogram of ash;

A_{500} is the ash yield at 500 °C.

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 concentration ranges of the trace elements in traded coals are listed in Table 1. The detection limits and precision required of methods are also listed.

Table 1 — Concentration ranges of trace elements in traded coals and indicated detection limits and precision required for analysis

Element	Range [a, b] mg/kg [c]	Required detection limit mg/kg [c]	Required precision [d] mg/kg [c]
As	0,5 to 5,0	0,1	0,1
B	5 to 400	5	5
Be	0,1 to 20	0,1	0,1
Cd	0,05 to 0,090	0,01	0,005
Cl [e]	< 0,01 to 0,2 %	0,01 %	0,01 %
Co	0,5 to 30	1	1
Cr	0,5 to 60	1	1
Cu	0,5 to 50	1	1
F	20 to 500	50	10
Hg	0,01 to 1,0	0,01	0,005
Mn	5 to 300	1	1
Mo	0,1 to 10	1	0,1
Ni	0,5 to 50	1	1
Pb	2 to 80	1	1
Sb	0,1 to 10	0,1	0,1
Se	0,2 to 10	0,1	0,1
Th	0,5 to 10	0,1	0,1
Tl	0,1 to 10	0,1	0,1
U	0,5 to 10	0,1	0,1
V	2 to 100	1	1
Zn	5 to 300	1	1

[a] From Swaine [15].

[b] The ranges are indicative only.

[c] Except where indicated as a percentage.

[d] The precision required is as indicated or 10 % relative (whichever is greater).

[e] Chlorine should be reported as a percentage.

9 Reporting of results

The results should be reported to the number of decimal places indicated in Table 2. The list of trace elements reported should be alphabetical by element symbol, with the exception of chlorine which has not traditionally been reported as a trace element.

Table 2 — Reporting of results

Element	Concentration range mg/kg [a]	Report to nearest mg/kg [b]
As, Sb, Se	0,1 to 10	0,1
B	5 to 50	5
	> 50	10 % relative
Be	0,1 to 10,0	0,1
Cd, Hg	0,01 to 0,10	0,01
Cl	0,01 % to 0,15 %	0,01 %
F	< 100	1
	100 u C_F < 500	5
Co, Cr, Cu, Mn, Ni, Tl, Zn	1 to 10	0,1
	> 10	10 % relative
Pb	4,5 to 9,5	0,1
Th, U	0,1 to 10	0,1

[a] Except where indicated as a percentage.

[b] Unless otherwise indicated.

10 Precision

The precision of the measurement should be as listed in Table 1.

11 Test report

The test report should contain the following information:

a) complete identification of the sample tested;

b) reference to the method used;

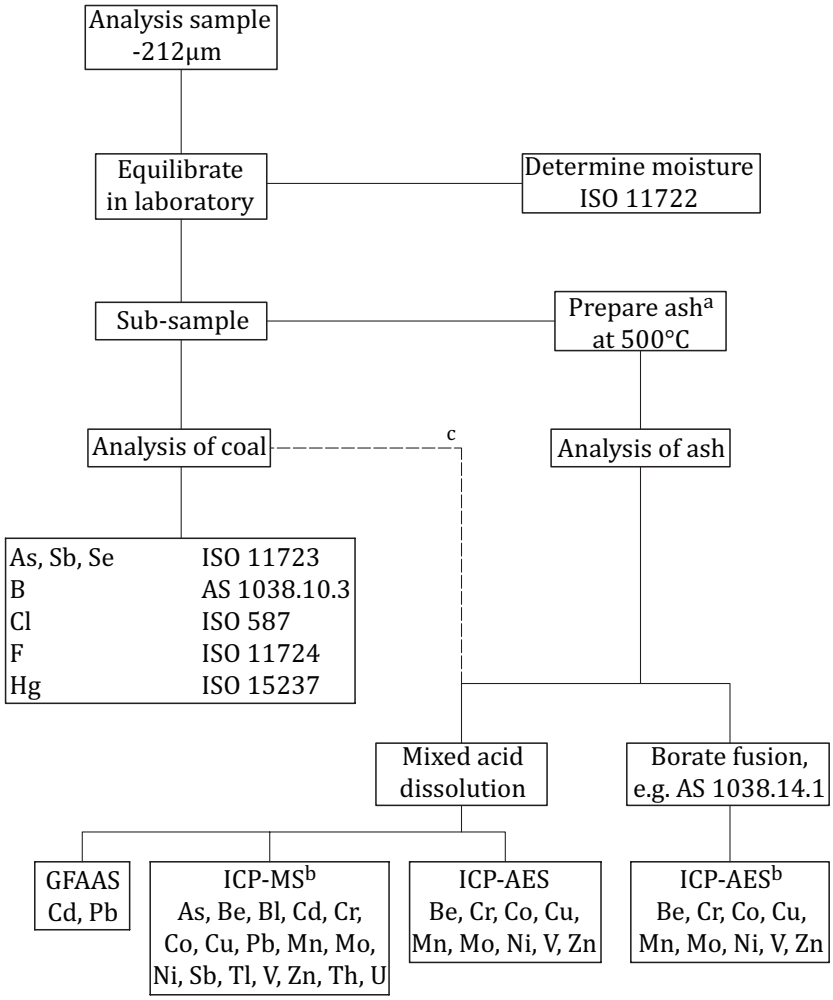
c) concentration of each trace element in the coal, expressed in milligrams per kilogram;

d) basis for reporting, e.g. air-dried basis;

e) air-dried moisture of the coal.

Annex A
(informative)

Scheme of analysis for trace elements



a If ash is sub-sampled for analysis, the percentage ash is determined to enable calculation of results to a coal basis.

b It is possible to use a diluted solution obtained by borate fusion for measurement by ICP-MS if the sensitivity obtained is equal to or better than that listed in Table 1.

c The scheme of analysis depicts by a broken line the dissolution of coal using mixed acids. This is an alternative to the ashing of coal prior to dissolution.

NOTE The accuracy of the procedures depicted can be ascertained by the analysis of appropriate CRMs.

Figure A.1 — Scheme of analysis for trace elements

Annex B
(informative)

Alternative dissolution procedures for coal

Procedures described in other standards and in the scientific literature (see Bibliography) may be used to digest both coal and coal ash to prepare solutions that may be used for the measurement of trace elements by a number of different analytical techniques such as ICP-AES and ICP-MS.

Most procedures require dissolution of coal ash by fusion or with an acid mixture including hydrofluoric acid. Most procedures that could be used for the dissolution of coal also require the use of hydrofluoric acid in acid mixture and the use of H_2O_2 to oxidize the carbonaceous matter of coal, e.g. CEN/TS 15297[13]. One coal-dissolution procedure that does not require the use of hydrofluoric acid is that of Wang et al.[16]

The necessity for the use of hydrofluoric acid is vigorously debated. The point of contention is whether all the analytes are released from the mineral matrix in the absence of this acid. Wang et al.[16] report that at the high temperatures and pressures obtained in the microwave-based procedure used, there is no requirement for hydrofluoric acid.

Also debated is the relative advantages and disadvantages of methods based on the dissolution of coal and those that require ashing of the coal before dissolution of the ash.

There are some advantages in the direct acid dissolution of coal to obtain solutions in which the analytes can be measured. The critical question is whether all the analytes are released from the carbonaceous matter of the coal during the digestion with mixed acids and H_2O_2. Conversely, the argument is put that ashing of coal may result in contamination and also the possible loss of some trace elements. Contamination is a risk for all procedures used in the analysis for trace elements and this risk must be managed. It is possible for some loss of some trace elements during ashing. Certainly the trace elements such as B, Hg, Se, and the halogens are lost (volatile) during ashing. There does not appear to be any loss of the other trace elements of interest during the ashing of coal at less than or equal to 500 °C.

No specific methods are prescribed in this International Standard. The onus is on the analytical chemist to use procedures that have been verified by the analysis of appropriate CRMs (i.e. of coal and coal ash). It is obviously prudent to confirm that all stages of the procedure adopted do not pose an unacceptable risk of contamination or loss of analytes. For example, if analytes are not recovered from the dissolution of a coal CRM or alternatively are lost during the ashing of a coal CRM, then the procedure is not appropriate for the determination of those analytes.

Bibliography

[1] ISO 587, *Solid mineral fuels — Determination of chlorine using Eschka mixture*

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

[3] ISO 11723, *Solid mineral fuels — Determination of arsenic and selenium — Eschka's mixture and hydride generation method*

[4] ISO 11724, *Solid mineral fuels — Determination of total fluorine in coal, coke and fly ash*

[5] ISO 15237, *Solid mineral fuels — Determination of total mercury content of coal*

[6] ISO 15238, *Solid mineral fuels — Determination of total cadmium content of coal*

[7] AS 1038.10.3, *Coal and coke — Analysis and testing — Determination of trace elements — Coal and coke — Determination of boron content — ICP-AES method*

[8] AS 1038.14.1, *Coal and coke — Analysis and testing — Higher rank coal ash and coke ash — Major and minor elements — Borate fusion/flame atomic absorption spectrometric method*

[9] ASTM D4208, *Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method*

[10] ASTM D6357, *Test Methods for Determination of Trace Elements in Coal, Coke, & Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, & Graphite Furnace Atomic Absorption Spectrometry*

[11] ASTM D6414, *Standard Test Methods for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption*

[12] ASTM D6722, *Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis*

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