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Solid mineral fuels — Determination of extractable metals in dilute hydrochloric acid

Combustibles minéraux solides — Détermination des métaux extractibles dans l'acide chlorhydrique dilué

Reference number
ISO 1952:2008(E)

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 1952 was prepared by Technical Committee ISO/TC 27, *Solid mineral fuels*, Subcommittee SC 5, *Methods of analysis*.

This second edition cancels and replaces the first edition (ISO 1952:1976), which has been technically revised.

Introduction

Sodium, potassium, calcium, iron and magnesium are commonly present in solid mineral fuel. They can contribute significantly to coal-utilization problems, such as boiler-tube fouling and ash disposal; they also affect product quality and gaseous emissions from combustion processes.

Research indicates that the amounts of alkaline and earth-alkaline metals extractable with dilute hydrochloric acid are more closely related to the fouling/slagging properties of solid mineral fuel than are the total amounts of the metals.

INTERNATIONAL STANDARD **ISO 1952:2008(E)**

Solid mineral fuels — Determination of extractable metals in dilute hydrochloric acid

1 Scope

This International Standard describes the extraction from solid mineral fuels by dilute hydrochloric acid and determination of extractable sodium, potassium, calcium, iron and magnesium.

2 Normative references

The following referenced documents are indispensable for the application 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 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 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

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*

3 Principle

A portion of the sample is extracted with hot, dilute hydrochloric acid after wetting of the solid mineral fuel with alcohol. All forms of sodium, potassium, magnesium, calcium, iron that are exchangeable or extractable with the hydrochloric acid are extracted from the coal. After removal of the residual solid mineral fuel by filtration, the concentrations of the elements in the filtrate are determined by atomic absorption spectrometry.

The concentrations of the elements may also be determined by ICP-OES if the instrument has been validated for the quantification in an appropriate manner.

4 Reagents and materials

Use analytical reagent grade chemicals. Other grades can be used, provided it is documented that the reagent is of sufficiently high purity to permit its use without adversely affecting the accuracy of the determination.

4.1 Water, high-purity deionized water as defined in ISO 3696, or as defined by the equivalent national standard.

4.2 Ethanol.

4.3 Hydrochloric acid (HCl).

4.4 Hydrochloric acid, concentrated, ρ_{20} = 1,19 g/ml.

4.5 Hydrochloric acid solution, prepared by mixing 1 part concentrated hydrochloric acid (4.4) with 1 part deionized water (4.1).

DANGER — The addition of the strong acid, HCl, to water liberates a significant amount of heat and can cause a violent reaction.

4.6 Nitric acid (HNO_3), concentrated, ρ_{20} = 1,42 g/ml.

4.7 Lanthanum oxide (La_2O_3).

4.8 Lanthanum solution.

Dissolve 23,4 g of La_2O_3 (4.7) in 350 mL of deionized water (4.1). Slowly add 50 mL of concentrated nitric acid. Stir until solution is completely mixed, transfer to a 1 l volumetric flask, dilute to the mark with water.

DANGER — The addition of the strong acid, HNO_3, to water liberates a significant amount of heat and can cause a violent reaction.

NOTE The lanthanum solution is used as an ionization suppressant during calcium determination. It is possible to use other commonly used ionization suppressants, e.g. cesium, as a alternative.

4.9 Magnesium perchlorate, anhydrous, −2,0 mm +0,7 mm, used as a desiccant.

DANGER — Regeneration of magnesium perchlorate by oven drying should not be attempted because of the risk of explosion. Magnesium perchlorate is a strong oxidant, and should be kept away from organic materials such as oils, greases and organic solvents.

4.10 Stock solutions

4.10.1 Sodium chloride (NaCl).

4.10.2 Sodium solution, 1 000 mg/L.

Dissolve 2,542 g of sodium chloride (4.10.1) (previously dried at 110 °C for 1 h) in 200 mL of deionized water (4.1), stir until solution is completely mixed, transfer to a 1 l volumetric flask, dilute to the mark with water.

4.10.3 Potassium chloride (KCl).

4.10.4 Potassium solution, 1 000 mg/L.

Dissolve 1,907 g of potassium chloride (4.10.3) (previously dried at 110 °C for 1 h) in 200 ml of water (4.1), transfer to a 1 l volumetric flask, dilute to the mark with water.

4.10.5 Calcium carbonate ($CaCO_3$).

4.10.6 Calcium carbonate solution, 1 000 mg/L.

Dissolve 2,497 g of calcium carbonate (4.10.5) (previously dried at 110 °C for 1 h) in a solution containing 10 ml of concentrated hydrochloric acid (4.4) and 200 ml of deionized water (4.1), stir until solution is completely mixed. Bring to a gentle boil to remove excess carbon dioxide. Cool the solution, transfer to a 1 l volumetric flask, dilute to the mark with water.

4.10.7 Magnesium oxide.

4.10.8 Magnesium solution, 1 000 mg/L.

Place 1,658 g of magnesium oxide (4.10.7) (previously heated at 1 000 °C for 1 h) in solution containing 10 ml of concentrated hydrochloric acid (4.4) and 200 ml of deionized water (4.1), stir until solution is completely mixed. Warm until dissolved, cool, transfer to a 1 l volumetric flask, dilute to the mark with water.

4.10.9 Iron, minimum purity 99,8 % Fe.

4.10.10 Iron solution, 1 000 mg/L.

Place 1,000 g of pure iron (4.10.9) in a solution containing 20 ml of concentrated hydrochloric acid (4.4) and 20 ml of deionized water (4.1), stir until solution is completely mixed. Heat to boiling and gently simmer until dissolved. Cool, transfer to a 1 l volumetric flask, dilute to the mark with deionized water.

4.10.11 Commercial stock solutions, optional, certified stock solutions with a concentration of the ion of interest of 1 000 mg/l that can be used as an alternative to preparing stock solutions.

4.11 Calibration solutions, prepared with the volumes of reagents given in Table 1.

Prepare calibration solution A, by adding 40 ml of lanthanum solution (4.8) and 32 ml of hydrochloric acid solution (4.5) to a 1 l volumetric flask. Add 1 ml of each stock solution and stir until the solution is completely mixed. Dilute to the mark with water.

Prepare calibration solutions B, C, D, E and the calibration BLANK in the same way as calibration solution A using the volumes of each stock solution shown in Table 1.

Additional calibration solutions within the range of those described here may be prepared in the same manner, in order to increase the number of points on the calibration graph. This can be necessary because of the wide ranges of analyte concentrations likely to be encountered, and also because of the variations in spectrometer responses.

The calibration solutions should be stored in screw-top polyethylene bottles. They should be discarded after three months.

Table 1 — Volumes of reagents for calibration solutions

Calibration solution	**Concentration of calibration solution** mg/l	**Volume of stock solution** ml	**Volume of lanthanum solution** ml	**Volume of hydrochloric acid solution** ml
A	1	1	40	32
B	2	2	40	32
C	3	3	40	32
D	4	4	40	32
E	5	5	40	32
BLANK	0	0	40	32

4.12 Filter paper, medium-textured filter paper.

5 Apparatus

5.1 Dispensers for reagents, with the following capacities:

5.1.1	for ethanol	5 ml, graduated.
5.1.2	for hydrochloric acid	10 ml, graduated to fit on top of the hydrochloric acid container.
5.1.3	for lanthanum solution	10 ml.

5.2 Hotplate.

5.3 Atomic absorption spectrometer.

5.4 Desiccator, with desiccant.

5.5 Plastic bottles, polyethylene or polypropylene with screw caps, giving an airtight seal, for storage of all solutions.

Condition the bottles before use, by filling with nitric acid (4.6) diluted 1 + 9. Allow to stand for at least 48 h. Rinse the bottles thoroughly with water.

5.6 Glassware, 250 ml beaker and 250 ml volumetric flask.

6 Preparation of the test sample

The sample shall be the general test sample prepared in accordance with ISO 13909-4 or ISO 5069-2.

7 Procedure

7.1 Preparation of test portion

Weigh approximately 1,5 g of the test sample to the nearest 2 mg into a 250 mL glass beaker. Concurrently, determine moisture in accordance with ISO 5068-2 or ISO 11722.

7.2 Preparation of test solution

Add 4 ml of ethanol to a glass beaker. Make a paste of the solid mineral fuel, stirring with a glass rod until the sample is thoroughly wetted. Do not remove the stirring rod. Add 50 ml of deionized water to the beaker. Add 8 ml of the hydrochloric acid solution (4.5) to the beaker.

Bring the solution to a boil. Heat at just below boiling for 15 min on a hotplate. Cover with a watch glass. Heat at just below boiling for a further 45 min. Care should be taken to maintain the volume in the beaker at approximately 50 ml with deionized water throughout the digestion. Cool, without swirling.

NOTE This procedure ensures that all of the ethanol is removed.

Filter the sample by decantation into a 250 ml volumetric flask through a filter paper. Rinse the beaker and stirring rod with hot hydrochloric acid solution, taking care to transfer all the contents onto the filter paper. Rinse the filter paper three times with about 20 ml portions of hot, hydrochloric acid solution.

Cool the flask, then add 10 ml of lanthanum solution to the flask. Make the flask up to volume with deionized water and mix thoroughly.

A blank test solution, which contains all the analytical reagents present in the test solution, shall be prepared by the same procedure as the test solution.

7.3 Analysis of test solutions

The atomic absorption spectrometer shall be prepared for operation in accordance with the manufacturer's instructions. Recommended gases and wavelengths are given in Table 2.

Table 2 — Recommended fuel and wavelength for the element analysed

Element	Wavelength nm	Oxidant — Fuel
K	766,5	air-C_2H_2
Na	589,6	air-C_2H_2
Mg	285,2	air-C_2H_2
Ca	422,7	air-C_2H_2
Fe	372,2; 248,3	air-C_2H_2

Deionized water shall be aspirated between each solution absorbance reading in order to clean the nebulizer/burner system and monitor baseline drift.

Periodically recalibrate using the standard solutions.

Prepare calibration graphs by plotting the absorbance versus the concentration of the calibration solutions and blank before analyses are performed.

From the plot of absorbance response versus concentration for each calibration solution, determine the concentration of the test solution. Record the concentration as c_x.

If the absorbance of the test solution exceeds the maximum absorbance of the calibration solutions, dilute the test solution to give an absorbance approximately equal to the mid-range absorbance of the calibration plot. Record the dilution factor as F_D. Measure the absorbance of the diluted test solution. From the plot of absorbance response for each calibration solution versus concentration, determine the concentration of the test solution. Record the concentration as c_x.

The five extractable metals can also be determined by ICP-OES if the instrument has been validated for the quantification in an appropriate manner.

8 Expression of results

For reporting, the concentration on a dry-sample basis, C_d, expressed in percent mass fraction, can be calculated from the concentrations determined in the test solutions as given in Equation (1):

$$C_d = (2{,}5 \times c_x \times F_D)/[m_s \times (100 - M_s)] \qquad (1)$$

where

F_D is the dilution factor;

c_x is the concentration of element x in the test solution, expressed in milligrams per litre;

m_s is the mass of the test sample, expressed in grams;

M_s is the moisture content of the test sample, expressed in percent mass fraction.

9 Precision

9.1 Repeatability

Repeatability shall be based on the results of duplicate determinations carried out over a short period of time but not simultaneously in the same laboratory by the same operator with the same apparatus.

Repeatability shall be calculated from the results obtained on two different test solutions prepared from representative portions of the general test sample. The results shall be calculated to a dry-coal basis as specified in Clause 8 to determine conformity to the repeatability conditions specified in Table 3.

If the absolute value of the difference in results calculated to a dry coal basis is greater than the repeatability values shown in Table 3, then one or both of the results is considered suspect. In the case where one or more of the results is suspect, refer to the section of ISO 5725-6:1994, Clause 6.

9.2 Reproducibility

Reproducibility shall be based on the results carried out in different laboratories by different operators with different apparatus.

Reproducibility shall be calculated from the results obtained on test solutions prepared from representative portions of the general analysis sample taken from the same bulk sample after the last stage of reduction. The results shall be calculated to a dry coal basis as specified in Clause 8 to determine conformity to the reproducibility conditions specified in Table 3.

If the absolute value of the difference in results calculated to a dry-coal basis is greater than the reproducibility values shown in Table 3, then one or both of the results is considered suspect. In the case where one or more of the results is suspect, refer to ISO 5725-6:1994, Clause 6.

Table 3 — Precision

Element concentration % mass fraction	**Repeatability**	**Reproducibility**
$\leqslant 0,5$	0,025 % mass fraction	0,05 % mass fraction
$> 0,5$	5 % of mean	10 % of mean

10 Test report

The test report shall include the following:

a) reference to this International Standard: ISO 1952:2008;

b) identification of the sample tested;

c) results of the determination;

d) date of the test.

ICS 73.040

Price based on 6 pages