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Carbonaceous materials for the production of aluminium — Petroleum coke — Determination of trace metals by inductively coupled plasma atomic emission spectrometry

Produits carbonés pour la production de l'aluminium — Coke de pétrole — Détermination des métaux à l'état de trace par spectrométrie d'émission atomique avec plasma induit par haute fréquence

Reference number
ISO 14435:2005(E)

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Contents

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.

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 14435 was prepared by Technical Committee ISO/TC 226, *Materials for the production of primary aluminium*.

Introduction

The presence and concentration of various metallic elements in a petroleum coke are major factors in determining the suitability of the coke for various end-uses. Users of petroleum coke require a standard procedure to determine the concentrations of these metallic elements in a coke sample. This International Standard describes such a procedure.

This International Standard is based on ASTM method D5600-98, published under the jurisdiction of ASTM Committee D2 on Petroleum Products and Lubricants and Subcommittee DO2.05.01 on Petroleum Coke Sampling and Procedures.

The repeatability and reproducibility information is based on an interlaboratory trial, which is reported in Research Report D02-1007 available from ASTM Headquarters.

INTERNATIONAL STANDARD **ISO 14435:2005(E)**

Carbonaceous materials for the production of aluminium — Petroleum coke — Determination of trace metals by inductively coupled plasma atomic emission spectrometry

WARNING — This International Standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard applies to carbonaceous materials for the production of aluminium.

This International Standard describes a test method which covers the analysis for commonly determined trace metals in test specimens of raw and calcined petroleum coke by inductively coupled plasma atomic emission spectroscopy. It can also be applied to other heat-treated carbonaceous materials e.g. coal-tar pitch coke, anthracite.

Elements to which this test method applies are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer.

This test method is applicable only to samples containing less than a mass fraction of 1 % ash.

Elements present at concentrations above the upper limit of the working ranges can be determined with additional, appropriate dilutions.

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 6375, *Carbonaceous materials for the production of aluminium — Coke for electrodes — Sampling*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
petroleum coke
solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions and cracked stocks

3.2
coal-tar pitch coke
solid, carbonaceous residue produced by decomposition of coal-tar pitch

3.3
gross sample
original, uncrushed, representative portion taken from a shipment or lot of coke

4 Principle

A test sample of the petroleum coke is ashed at 700 °C.

The ash is fused with lithium borate. The melt is dissolved in dilute nitric acid (HNO_3), and the resultant solution is analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using simultaneous, or sequential, multi-elemental determination of elements. The solution is introduced to the ICP instrument by free aspiration or by an optional peristaltic pump. The concentrations of the trace metals are then calculated by comparing the emission intensities from the sample with the emission intensities of the standards used in calibration.

5 Interferences

For spectral interferences, follow the instrument manufacturer's operating guide to develop and apply correction factors to compensate for the interferences. To apply interference corrections, all concentrations shall be within the previously established linear-response range of each element.

NOTE Spectral interferences are caused by

a) overlap of a spectral line from another element,

b) unresolved overlap of molecular band spectra,

c) background contribution from continuous or recombination phenomena, and

d) stray light from the line emission of high-concentration elements.

Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high amounts of dissolved solids or high acid concentrations. If physical interferences are present, they shall be reduced by diluting the sample, by using a peristaltic pump, or by using the standard-additions method. Another problem that can occur with high amounts of dissolved solids is build-up of salts at the tip of the nebulizer, which can affect aerosol flow rate and cause instrumental drift. This problem can be controlled by wetting the argon prior to nebulization by using a tip washer, or diluting the sample.

Table 1 — Elements determined and suggested wavelengths

Element	Wavelengths nm[a,b]	Concentration range µg/g[c]
Aluminium	237,313 256,799 308,215 396,152	15 to 110
Barium	455,403 493,410	1 to 65
Calcium	317,933 393,367 396,847	10 to 140
Iron	259,940	40 to 700
Magnesium	279,079 279,553	5 to 50
Manganese	257,610 294,920	1 to 7
Nickel	231,604 341,476 352,454	3 to 220
Silicon	212,412 251,611 288,159	60 to 290
Sodium	588,995 589,592	30 to 160
Titanium	334,941 337,280	1 to 7
Vanadium	292,402	2 to 480
Zinc	202,548 206,200 213,856	1 to 20

[a] The wavelengths listed were utilized in the interlaboratory trial because of their sensitivity. Other wavelengths can be substituted if they can provide the required sensitivity and are treated with the same corrective techniques for spectral Interference (see Clause 5). In time, other elements may be added as more information becomes available and as required.

[b] Alternative wavelengths can be found in references such as *Inductively Coupled Plasma Atomic Emission Spectroscopy*, Winge, R.K., Fassel, V.A., Peterson, V.J., and Floyd, M.A., Elsevier, 1985.

[c] Based on this interlaboratory trial. This method can be applicable to other elements or concentration ranges, but precision data are not available.

6 Apparatus

6.1 Balance, top loading, with automatic tare, capable of weighing to 0,000 1 g, of capacity 150 g.

6.2 Ceramic cooling plate, desiccator plates have been found to be effective.

6.3 Crucible support, nichrome wire triangles.

6.4 Furnaces, electric, capable of temperature regulation at 700 °C ± 10 °C and 1 000 °C ± 10 °C, with allowances for exchange of combustion gases and air.

6.5 Inductively coupled plasma atomic emission spectrometer, either a sequential or simultaneous spectrometer is suitable, equipped with a quartz ICP torch and radio frequency (RF) generator to form and sustain the plasma.

6.6 Magnetic stirring bars, polytetrafluoroethylene (PTFE) coated, approximately 12 mm in length.

6.7 Magnetic stirring hotplate.

6.8 Meker-type forced air burner.

6.9 Nebulizer, a high-solids nebulizer is recommended.

6.10 Peristaltic pump, a peristaltic pump is recommended.

6.11 Platinum dish, of capacity 50 ml to 58 ml, recommended type Pt II (Pt containing 5 % mass fraction Au).

6.12 Platinum dish, of capacity 100 ml to 200 ml, recommended type Pt II.

6.13 Platinum-tipped tongs.

6.14 Ring stand, with crucible support.

6.15 Sieves, 0,250 mm and 0,075 mm, conforming to ISO 3310-1.

6.16 Tungsten carbide mill, laboratory size.

6.17 Vacuum filtration apparatus.

6.18 Filter paper, sized to fit a vacuum filtration apparatus, of fine porosity, slow flow rate, 2,5 µm particle retention.

6.19 Ultrasonic bath.

7 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and distilled or demineralized water, or water of equivalent purity.

7.1 Water, complying with grade 2 of ISO 3696:1987.

7.2 Argon gas supply, welding grade.

7.3 Lithium metaborate ($LiB0_2$), powder (high purity) or **lithium tetraborate** ($Li_2B_40_7$), powder (high purity).

The use of a blend containing 66 % lithium metaborate ($LiB0_2$) and 34 % lithium tetraborate ($Li_2B_40_7$) is recommended: a commercially available product is known as "Spectromelt A12“[1].

7.4 Nitric acid, 65 % mass fraction (high purity).

7.5 Solution No. 1, nitric acid, prepared by diluting 400 ml of concentrated HNO_3 (65 % mass fraction) to 2 000 ml with water.

NOTE The mass fraction of concentrated HNO_3 is 65 %. The dilution of 400 ml HNO_3 (65 % mass fraction) to 2 000 ml with water gives a mass fraction of 13 % HNO_3 with a density of 1,072. The result is a mass fraction of 12,1 %.

7.6 Solution No. 2, standard and sample solution additive.

Weigh 20 ± 0,1 g, of lithium borate into a 100 ml to 200 ml platinum dish. Place in a furnace at 1000 °C for 5 min, to fuse to a liquid. Remove and cool. Place the cooled platinum dish containing the fused recrystallized lithium borate and a magnetic stirring bar (6.6) into a 2 litre glass beaker. Add 1 000 ml of Solution No. 1. Heat gently and stir the solution on the magnetic stirring hotplate (6.7) until the lithium borate completely dissolves. After dissolution, remove the platinum dish with a glass rod. Rinse the platinum dish and glass rod with water into the lithium borate solution. Immediately transfer the warm solution quantitatively to a 2 litre volumetric flask. Dilute to about 1 800 ml with water to avoid crystallization. Mix the solution and cool to room temperature. Dilute to volume with water, mix thoroughly, and vacuum-filter the entire solution through filter paper.

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[1] Spectromelt A12 is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

50 ml of Solution No. 2 contains exactly 0,5 g of lithium borate and 25 ml of Solution No. 1.

7.7 Standard stock solutions, use certified ready-to-use single- or multi-element standard stock solutions with a concentration of 1 000 µg/ml for each element in nitric acid.

CAUTION — To minimize the potential of contamination, prepare the platinum ware by boiling in dilute HNO_3 [5 % HNO_3 (volume fraction) + 95 % water (volume fraction)] and rinsing thoroughly with water. After this initial cleaning, handle the platinum ware with clean platinum-tipped tongs and protect from all sources of contamination. Similarly, clean all glassware used in the analyses with acid.

8 Sample preparation

Take a sample in accordance with ISO 6375.

8.1 Crush and divide the sample to obtain a laboratory analysis sample. Crush to pass through a 0,250 mm sieve.

8.2 Use a tungsten-carbide mill to crush an approximately 30 g representative test portion of the minus 0,250 mm sieve analysis sample to pass through a 0,075 mm sieve. Dry this test portion to constant mass at 110 °C to 115 °C and store in a desiccator until it is cool and needed for the analysis. The drying procedure may be omitted if less precision is required. Drying to constant mass is recommended. Report whether the test portion was dried or undried.

Take care to ensure that the preparation of the minus 0,075 mm analysis samples, from the minus 0,250 mm analysis samples, neither removes metals through loss nor increases metals through contamination.

9 Preparation of apparatus

9.1 ICP-AES instrument

Consult the manufacturer's instructions for operation of the inductively coupled plasma atomic emission spectrometer.

9.2 Peristaltic pump

When a peristaltic pump is used, inspect the pump tubing and replace it, as necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

9.3 ICP excitation source

Initiate the plasma source at least 30 min before performing the analysis. It is recommended that the source be initiated 60 min before performing the analysis. Some instrument manufacturers recommend even longer warm-up periods.

9.4 Wavelength profiling

Perform any wavelength profiling that is required in the normal operation of the instrument.

9.5 Operating parameters

Assign the appropriate operating parameter to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (optional), inter-element correction factors (optional), integration time, and internal standard correction (optional).

9.6 Sensitivity, calibration and concentration ranges

Each analyst shall determine the sensitivity and linear range of calibration of their own equipment and choose concentration ranges for standards compatible with the samples and instrument specific to their own work. Sample dilutions can be required for the determination of some elements (see 10.6).

9.7 Linear response range

The linear response range shall be established for each particular instrument being used. This is accomplished by running intermediate standards between the blank and the calibration standard and by running standards containing higher concentrations than the calibration standard within the linear range of response.

10 Procedure

10.1 Weigh 5 g, to the nearest 0,1 mg, of the dried, or undried, petroleum-coke test portion prepared in Clause 8 into a labelled 50 ml to 58 ml platinum dish.

10.2 Place the platinum dish in a cold muffle furnace and heat directly to 700 °C ± 10 °C until all carbonaceous matter is removed. Transfer the platinum dish to a desiccator and cool to room temperature. Record the mass of the platinum dish to determine the total mass of ash in the sample.

NOTE If the total mass of ash in the sample exceeds 50 mg, the ashing procedure is not applicable (mass fraction of ash in the sample > 1 %, see third paragraph of Clause 1). This is because it is not possible to dissolve more than 50 mg of the ash in 500 mg of the melt, and to dissolve more than 500 mg of the melt in a 100 ml volumetric flask.

10.3 Convert the ash into a solution by using one of the following methods:

a) Weigh, using the analytical balance (6.1), onto a tared weighing paper, 0,5 g (± 0,005 g) of lithium borate powder. Sprinkle the lithium borate evenly over the ash. Use platinum-tipped tongs to place the platinum dish in a muffle furnace at 1 000 °C ± 10 °C for 1 min or 2 min. Use the platinum-tipped tongs to gently swirl the melt to dissolve the ash. Continue heating in the furnace for 2 min to 3 min or until a clear, transparent melt is obtained.

   The ideal fusion after cooling will look like clear glass inside the platinum dish. An opaque melt possibly indicates poor fusion and some of the ash can remain insoluble during the dissolution step. Full dissolution of the ash is required.

The total heating time should be 4 min. If the melt is heated for more than 4 min, losses of sodium may occur. If it is heated for less than 4 min, some of the ash can remain undissolved.

b) If a 1 000 °C ± 10 °C furnace is not available, the fusion can be performed using a Meker-type burner as follows. Place the platinum dish onto the crucible support resting on a ring-stand over the burner, and adjust the forced-air gas flame so that the lithium borate melts in about 30 s. Using platinum-tipped tongs, gently swirl the melt to dissolve the ash. Continue heating over the burner for 2 min or 3 min, or until a clear, transparent melt is obtained.

10.4 Allow the melt to cool for 5 min to 10 min on a ceramic cooling plate, add 25 ml of Solution No. 1 and place immediately in the ultrasonic bath until the melt has completely dissolved. Keep the solution below 50 °C to avoid precipitation of hydrous silica. If some of the ash constituents (e.g. hydrous silica) precipitate, repeat the analysis.

10.5 Remove the dish from the ultrasonic bath, transfer the solution quantitatively to a 100 ml volumetric flask, rinse the dish into the flask with water, dilute to volume with water, and mix thoroughly.

10.6 Prepare any required dilution using Solution No. 2, diluted 1:1 with water.

10.7 Prepare a calibration standard using 50 ml of Solution No. 2 per 100 ml and containing the desired volume of standard stock solutions. Dilute with water.

NOTE Standard and sample solutions are of similar composition to minimize errors due to matrix effects.

10.8 Calibrate the ICP-AES instrument using the calibration standard prepared in 10.7 in accordance with manufacturer's directions.

10.9 Determine the concentration of each metal in the sample solution.

11 Calculation

Calculate the mass fraction of each metal, expressed as mg/kg (or in percent if multiplied by 10 000), in the sample as follows:

$$w_i = \frac{\rho_i \times V}{m} \times \frac{V_\mathrm{f}}{V_\mathrm{o}} \qquad (1)$$

where

w_i is the mass fraction of the metal being calculated, expressed as mg/kg;

ρ_i is the concentration of the metal in the solution analysed, expressed as mg/l;

V is the volume of sample solution, in ml;

m is the mass of the sample, in g;

$\frac{V_\mathrm{f}}{V_\mathrm{o}}$ is the dilution factor, if dilution of the sample solution is required to bring the metal concentrations into the range of standard solutions;

where

V_f is the final volume of diluted sample solution;

V_o is the initial volume of sample solution.

12 Test report

The test report shall include the following information:

a) details necessary for the identification of the material tested;

b) a reference to this International Standard;

c) whether a dried test portion or undried test portion was used;

d) the mass fraction for each element, expressed as mg/kg or mass percent (1 000 mg/kg = 0,1 %);

e) anything unusual observed during the analysis;

f) the date of the test.

13 Precision and bias for the dried test portion

The precision of this method is defined according to ASTM E691.

The repeatability and reproducibility are taken from Table 2.

Table 2 — Repeatability and reproducibility

Element	Repeatability	Reproducibility
Aluminium	$0{,}32 \cdot \bar{w}_{\mathrm{Al}}{}^{2/3}$	$0{,}92 \cdot \bar{w}_{\mathrm{Al}}{}^{2/3}$
Barium	$0{,}19 \cdot \bar{w}_{\mathrm{B}}{}^{2/3}$	$0{,}71 \cdot \bar{w}_{\mathrm{B}}{}^{2/3}$
Calcium	7,2	20,8
Iron	$1{,}66 \cdot \bar{w}_{\mathrm{Fe}}{}^{1/2}$	$3{,}77 \cdot \bar{w}_{\mathrm{Fe}}{}^{1/2}$
Magnesium	$0{,}21 \cdot \bar{w}_{\mathrm{Mg}}{}^{2/3}$	$0{,}61 \cdot \bar{w}_{\mathrm{Mg}}{}^{2/3}$
Manganese	$0{,}042 \cdot (\bar{w}_{\mathrm{Mn}} + 2.55)$	$0{,}34 \cdot (\bar{w}_{\mathrm{Mn}} + 2.55)$
Nickel	$0{,}52 \cdot \bar{w}_{\mathrm{Ni}}{}^{2/3}$	$0{,}96 \cdot \bar{w}_{\mathrm{Ni}}{}^{2/3}$
Silicon	$0{,}71 \cdot (\bar{w}_{\mathrm{Si}} + 4.80)$	$0{,}20 \cdot (\bar{w}_{\mathrm{Si}} + 4.80)$
Sodium	$1{,}04 \cdot \bar{w}_{\mathrm{Na}}{}^{1/2}$	$3{,}52 \cdot \bar{w}_{\mathrm{Na}}{}^{1/2}$
Titanium	0,75	1,16
Vanadium	$0{,}20 \cdot \bar{w}_{\mathrm{V}}{}^{3/4}$	$0{,}35 \cdot \bar{w}_{\mathrm{V}}{}^{3/4}$
Zinc	$1{,}07 \cdot \bar{w}_{\mathrm{Zn}}{}^{1/3}$	$2{,}20 \cdot \bar{w}_{\mathrm{Zn}}{}^{1/3}$
$\bar{w}_{\mathrm{Al}}$, $\bar{w}_{\mathrm{B}}$ … is the average value of two results, in mg/kg		

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[3] ASTM D5600-98, *Standard Test Method for Trace Metals in Petroleum Coke by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)*

[4] ASTM E691-99, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method*

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