INTERNATIONAL STANDARD

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Carbonaceous materials used in the production of aluminium — Green coke and calcined coke for electrodes — Analysis using an X-ray fluorescence method

Produits carbonés utilisés pour la production de l'aluminium — Coke calciné et coke cru pour électrodes — Analyse par fluorescence aux rayons X

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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 12980 was prepared by Technical Committee ISO/TC 47, *Chemistry*, Subcommittee SC 7, *Aluminium oxide, cryolite, aluminium fluoride, sodium fluoride, carbonaceous products for the aluminium industry*.

Introduction

The determination of the elemental impurities is important for reasons of metal quality and anode consumption. This International Standard refers only to petroleum coke although the principles described are valid for pitch, anthracite, graphite or electrode materials. As the sample preparation and/or the mass fraction ranges for these other materials are quite different it is intended that specific standard methods will be published for each material.

Carbonaceous materials used in the production of aluminium — Green coke and calcined coke for electrodes — Analysis using an X-ray fluorescence method

1 Scope

This International Standard specifies an X-ray fluorescence method for the determination of elemental impurities in green and calcined petroleum cokes used for the manufacture of anodes. These anodes are used in the production of aluminium.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these this publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

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

3 Principle

A pressed tablet of pulverized coke and organic binder is irradiated by X-rays from a target thin window X-ray tube. The X-ray tubes can be chromium, rhodium or scandium depending on which elements are to be determined.

Irradiation of the test specimen causes ejection and rearrangement of orbital electrons resulting in the emission of secondary radiation with a characteristic wavelength for each element.

This secondary radiation is reflected, onto the detector system, by a crystal, which is set at a specific angle to the secondary radiation. Only specific radiation which obeys Bragg's law reaches the detector system.

$$n\lambda = 2d \cdot \sin\theta \quad (1)$$

where

n is the order of the diffraction;

λ is the X-ray wavelength;

d is the interplanar distance in the crystal;

$\sin\theta$ is the angle setting of the crystal.

The intensities of the specific secondary radiation are calculated into mass fractions according to given calibration curves.

4 Apparatus and materials

4.1 X-ray fluorescence spectrometer, equipped with the following crystals: LiF_{200} (lithium fluoride, reflecting plane 200), PE (pentaerythiol), PX1 (synthetic W-Si), Ge, TIAP (thallium acid phthalate) and LSM (layered synthetic microstructure). For instruments equipped with a side window X-ray tube, a scandium tube is advantageous for light elements. For instruments equipped with an end window X-ray tube, a rhodium tube offers optimum sensitivity.

4.2 Swinging-disc mill, with tungsten-carbide grinding devices.

4.3 Organic binder, suitable for pressed-tablet preparation. The binder shall not contain any of the elements to be analysed. Suitable binders are 'Hoechst wachs G' or stearic acid.

4.4 Tablet press, capable of providing a 20-tonne load.

4.5 Appropriate sample holders, for example aluminium dishes or brass rings with the dimensions as shown in Figure 1.

4.6 Detector gas, consisting of 90 % argon and 10 % methane.

4.7 Calibration standards, commercially available and certified covering the range of mass fraction given in clause 6.5.

4.8 Reference samples (RS), commercially available and certified with appropriate mass fractions for all elements. (See 6.4.2)

Dimensions in millimetres

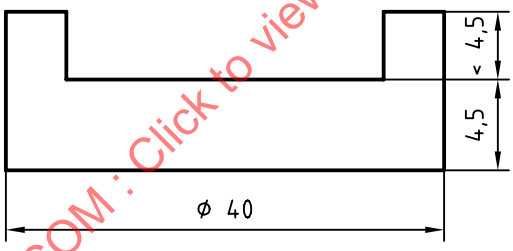

Figure 1 — Dimensions of sample holder

5 Sampling and test specimen preparation

5.1 Sampling

Sampling shall be in accordance with the requirements of ISO 6375.

5.2 Test specimen preparation

Crush the sample into sufficiently small particles so as to pass it through a 4 mm sieve. Dry to constant mass at 120 °C. Mill the sample of crushed material into sufficiently small particles so as to pass it through a 63 μm sieve. Mix approximately 30 g of this sieved material with approximately 5 g of binder and remill for 20 s. Crush any remaining lumps with a spatula.

If too many lumps are formed in this mixture, repeat the above procedure with a smaller quantity of binder, for example 4 g. When a smaller quantity of binder is used, test it to see if the calibration sample and other samples give pressed tablets strong enough to withstand the procedure. Repeat the above procedure until a suitable quantity of binder has been added to provide an acceptable mixture for pressing a tablet.

Place the material into the selected sample holder.

NOTE Aluminium dishes are preferred, but brass rings may also be used.

Place the filled sample holder in the press and press at 20 t for 20 s.

For the best results, the test specimen should be at least 4 mm thick.

6 Procedure

6.1 Measurement conditions

The measurement conditions are apparatus-dependent but the indications in Table 1 can serve as guidelines. Normally no line overlapping will be experienced if these conditions are used for the measurement of petroleum coke.

Table 1 — Typical measurement conditions for the different elements

Element line	Na K_α	Al K_α	Si K_α	S K_α	Ca K_α	V K_α	Fe K_α	Ni K_α
Crystal	LSM[a] or PX1	PE or PX1	PE or PX1	PE or Ge	LiF_{200}	LiF_{200}	LiF_{200}	LiF_{200}
Counter	F[b]	F	F	F	F	F	F	F
Exposure, total time, s	100	20	20	10	10	20	30	20
Collimator	coarse	coarse	coarse	medium	fine	fine	fine	fine
kV	40	40	40	40	40	40	60	60
mA	60	60	60	60	60	60	40	40
Angle	28°	PE: 145,1° PX1: 19,5°	PE: 109,2° PX1: 16,6°	PE: 75,8° PX1: 110,9°	113,1°	76,9°	57,5°	48,7°
Offset angle[c]	±2°	—	—	—	—	+1°	+1°	−1°

F = flow counter

a Layered synthetic microstructure with 2d value around 5 nm.

b A 1 μm or 2 μm flow counter window is required.

c Background measurement angles (± offset angles).

6.2 Intensities and background corrections

The net peak intensity I, expressed as the number of counts per second, of the element of interest is calculated as the difference between the measured peak intensity of the element and the background intensity at the peak angle in accordance with equations (4) and (5). See Figure 2.

$$I = I_p - I_b \quad (2)$$

where

I_p is the count rate, expressed as the number of counts per second, at the element position (2θ);

I_b is the background count rate, expressed as the number of counts per second, at the element position (2θ);

and

$$I = I_p - C_1 \cdot I_{b1} - C_2 \cdot I_{b2} \quad (3)$$

where

I_{b1} is count rate, expressed as the number of counts per second, at the negative (–) offset angle of the background position;

I_{b2} is count rate, expressed as the number of counts per second, at the positive (+) offset angle of the background position;

$$C_1 = \frac{d_2}{d_1 + d_2}$$

$$C_2 = \frac{d_1}{d_1 + d_2}$$

where

d_2 is the difference between the positive (+) offset angle of the background position and 2θ;

d_1 is the difference negative (–) offset angle of the background position and 2θ;

to give the net count rate I.

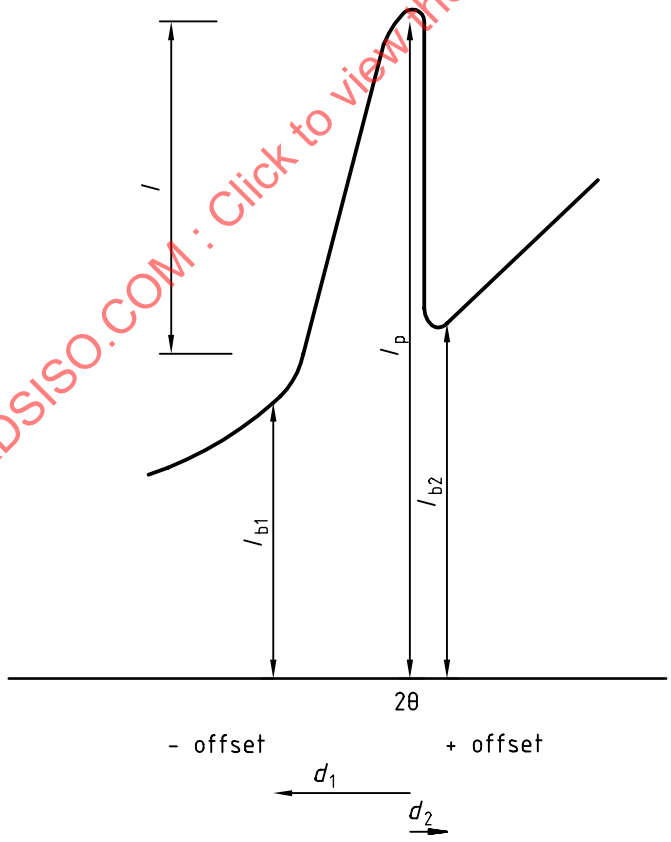

Figure 2 — Intensities and background corrections

6.3 Counting time

The minimum counting time is the time necessary to achieve a net counting error $(2\sigma_{\%})_{net}$ which is less than the desired precision for the measurement.

Assume that the part of the counting error in the repeatability ($\sim 4\sigma$) of this method is about 50 %.

Choose a reference material having an element mass fraction in the middle of the range given in 6.5.1. Measure the counting rate. Calculate the minimum counting time for each element by using equation (4).

$$t = \left(\frac{100}{2\sigma_{\%}} \times \frac{1}{\sqrt{I_p} - \sqrt{I_b}} \right)^2 \quad (4)$$

Where

t is the total counting time for the peaks and background;

I_p is measured peak intensity, expressed as the number of counts per second;

I_b is the background intensity, expressed as the number of counts per second;

$2\sigma_{\%}$ is the relative targeted precision, expressed as a percentage, at the 95 % probability level.

For Na, take 2 % as the relative targeted precision for $2\sigma_{\%}$. For other elements, take 1 % for $2\sigma_{\%}$.

This equation requires that the distribution of the counting time at peak and background follow the equation below:

$$\frac{t_p}{t_b} = \sqrt{\frac{I_p}{I_b}} \quad (5)$$

where

t_p is the counting time for the peak;

t_b is the counting time for the background.

NOTE Additional checks such as monitor samples are recommended, and will depend on the age and state of the equipment. A description is given in 6.4.1.

6.4 Drift detection by use of a monitor sample

6.4.1 Drift detection

Any drift in the net count rate can be detected by using a monitor standard during the calibration procedure and during the measurement of unknown samples.

Calculate the drift factor f_d for each element by the ratio

$$f_d = \frac{I_1}{I_n} \quad (6)$$

where

I_1 is the intensity of monitor standard during the calibration procedure;

I_n is the intensity of monitor standard when unknown samples are measured.

If the drift factor does not lie within the repeatability range (see 7.1) this indicates that a major change, or problem has occurred in the X-ray equipment. Check the X-ray equipment, rectify as necessary and recalibrate.

6.4.2 Selection and preparation of monitor standards

A monitor standard can be prepared as described below or, alternatively, use a reference sample (RS), with appropriate mass fractions for all elements.

Monitor standards can be prepared in copper dishes, with dimensions according to the actual sample holder as shown in Figure 1.

Select appropriate components for the monitor sample, weigh them into the desired proportions, mix them carefully and fuse them at 1 200 °C in a (Pt + 5 % Au)-crucible (a typical recipe is given in Table 2).

Allow to cool, crush the melt and melt again. Repeat this procedure once more, then finely grind the melt in the swinging-disc mill. Place the powder in a thin layer in the copper dish and heat on a gas burner until the enamel softens and adheres to the copper. Repeat this procedure until a layer of 0,5 mm in the copper dish is created. A typical recipe for monitor standards is shown in Table 2. A suitable amount is 5 g.

Table 2 — Typical monitor recipe

	S	V	Ni	Na	Ca	Al	Fe	Si
$Li_2B_4O_7$	K_2SO_4	V_2O_5	NiO	Na_2CO_3	CaO	Al_2O_3	Fe_2O_3	SiO_2
90 %	8 %	0,3 %	0,3 %	0,2 %	0,2 %	0,2 %	0,3 %	0,3 %

It is preferable that the monitor standard gives somewhat higher intensities than the test samples.

The best results are obtained when the mass fractions of the different elements are chosen in such a way that the monitor intensities are 10 times to 20 times the mean intensities measured on the calibration standards.

Take the monitor sample, as described above, or the appropriate reference sample that is to be used as a monitor, and prepare according to 5.2.

After calibration, in order to determine its nominal mass fraction, test the homogeneity of the monitor standard.

If the actual value of the monitor RS lies outside the repeatability range (see 7.1) when analysing unknown samples, analyse a new RS. If the results still exceed the tolerance mass fraction, recalibrate the equipment.

6.5 Calibration

6.5.1 Reference material selection

The certified reference materials are selected in order to cover the range of impurities given in Table 3.

Table 3 — Mass fraction range of the reference materials

Elements	**S** %	**V** µg/g	**Ni** µg/g	**Na** µg/g	**Ca** µg/g	**Al** µg/g	**Fe** µg/g	**Si** µg/g
Mass fraction range	0,5 to 5	20 to 500	20 to 500	20 to 200	20 to 200	20 to 500	20 to 500	20 to 500