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Carbonaceous materials used in the production of aluminium — Pitch for electrodes — Determination of volatile matter content

Produits carbonés utilisés pour la production de l'aluminium — Brais pour électrodes — Détermination de la teneur en matière volatile

Reference number
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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 12977 was prepared by Technical Committee ISO/TC 47, *Chemistry*, Subcommittee SC 7, *Aluminium oxide, cryolite, aluminium fluoride, sodium fluoride, carbonaceous materials for the aluminium industry*.

Annex A of this International Standard is for information only.

Carbonaceous materials used in the production of aluminium — Pitch for electrodes — Determination of volatile matter content

1 Scope

This International Standard describes an empirical method for the determination of the volatile matter content of pitch by gas chromatographic analysis of its solution in toluene. Strict adherence to the procedure is essential because of the empirical nature of the method.

2 Normative references

The following normative documents contain 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 publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents 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 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 6257, *Carbonaceous materials used in the production of aluminium — Pitch for electrodes — Sampling.*

3 Term, definition and symbols

3.1 Term and definition

For the purposes of this International Standard, the following term and definition applies.

3.1.1
volatile matter content
total percentage by mass of those components present in the pitch which have gas-chromatographic retention times corresponding to atmospheric pressure boiling points up to 360 °C under the conditions used

3.2 Symbols, subscripts and superscripts

3.2.1 Symbols

A	surface area of the chromatographic peak
a	slope of the regression line
B	equivalent boiling point at atmospheric pressure
b	intercept of the regression line

F	factor to convert tabulated peak areas to the corresponding percentages by mass in the original pitch sample
K_A	ratio of areas of dibenzothiophene to phenanthrene
K_T	ratio of retention times
m	mass of calibrant compound
R	reproducibility
R_f	response factor for calibrant compounds (5.2)
r	repeatability
T	retention time of the chromatographic peak
w_d	percentage by mass of dibenzothiophene present in sample

3.2.2 Subscripts and superscripts

A, B, C	solutions A, B, C corresponding respectively to chromatograms A, B, C
d	dibenzothiophene
i	i-th peak
p	phenanthrene
pitch	pitch
T	retention time
tot	total surface area of calibrant compounds in the chromatogram
0	presence in the original pitch sample
$'$	contribution resulting from the addition of the dibenzothiophene internal standard

4 Principle

A calibration analysis of a multicomponent test mixture of pure compounds comprising selected major components of coal tar together with an internal standard component is performed by gas chromatography under defined conditions on a chromatographic column having a non-polar stationary phase.

The results of this analysis establish a substantially rectilinear relationship between the chromatographic retention times of the individual components of the mixture and their atmospheric pressure boiling points. In addition, the analysis provides a mean relative response factor which relates the ratio of the total mass to total chromatographic peak area for the selected calibrants to the equivalent ratio for the internal standard.

Because the selected internal standard compound, dibenzothiophene, is also a normal component of coal tar it is necessary to perform the ensuing chromatographic analysis of the pitch on two solutions, one with and one without addition of the internal standard, thus enabling the area to mass response of the chromatograph to the internal standard to be calculated.

From the latter figure and from the mean relative response factor for the components in the calibration test mixture the amounts of material represented by the peaks of the test sample analysis chromatogram are calculated. These data, together with the previously established relationship between the chromatographic retention time and the atmospheric pressure boiling points of the components, allow the construction of a simulated distillation curve or table of values for the test sample.

From these values, the sum of the percentages of components with atmospheric pressure boiling points up to and including 360 °C may be calculated by interpolation.

5 Reagents

WARNING — Refer to the reagent supplier's Health and Safety data sheets for the precautions which are to be taken for the safe use of the reagents listed under 5.1, 5.2 and 5.3.

5.1 Dibenzothiophene, of at least 98 % purity by mass.

5.2 Calibrant compounds1) comprising naphthalene, 2-methylnaphthalene, acenaphthene, dibenzofuran, fluorene, phenanthrene, fluoranthene and pyrene, all of which shall be of at least 98 % purity and none of which shall contain a measurable amount of any impurity which co-elutes with the dibenzothiophene (5.1) under the chromatographic conditions used.

NOTE Boiling points of the calibrant compounds are given in annex A.

5.3 Toluene, of analytical reagent quality.

6 Apparatus

Ordinary laboratory apparatus and the following.

6.1 Gas chromatograph, having a heated injector capable of operating at 300 °C, a flame-ionization detector and its associated amplifier, and equipped for use with capillary columns under programmed-temperature conditions from approximately 50 °C to 300 °C, with heating rates of 1 °C/min to 10 °C/min.

It is preferable that splitless injection is used. If any other arrangement is used, it shall be recorded in the test report (see clause 15).

6.2 Electronic integrator, designed for processing the signal from the gas chromatograph (6.1) to give the retention times and areas of the chromatographic peaks.

The integrator may be combined with the gas chromatograph (6.1) or may be a separate unit.

6.3 Capillary column, having a non-polar stationary phase with low-bleed characteristics under the chromatographic conditions used in the test.

When the column is operated under the selected analysis conditions without injection of a sample, the baseline of the chromatogram shall remain rectilinear without significant variation over the range of retention times which includes the retention times of naphthalene and pyrene.

NOTE 1 Typically the column will be of 12 m to 25 m length, constructed of fused silica capillary tubing having an internal diameter of 0,53 mm minimum, taking into account splitless injection and the injection volume selected (see clause 10).

The column shall have a chemically-bonded stationary phase of the poly(dimethylsiloxane) type.

NOTE 2 Other stationary phases which have the required low-bleed characteristics and give symmetrical peaks showing a similarly rectilinear relationship between the retention times and the boiling points of the calibrants listed in 5.2 are acceptable.

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1) "Calibrant" compounds are used as the reference materials for calibration.

6.4 Chromatographic syringes, of a type and capacity appropriate to the characteristics of the injection system of the gas chromatograph (6.1).

NOTE Typically the required capacity will be in the range 1 µl to 25 µl.

6.5 Volumetric flasks, conforming to the requirements of ISO 1042, of capacity 10 ml and 100 ml.

6.6 Ultrasonic bath, of a type designed for general laboratory use.

NOTE Typically this will have a power rating of 100 W to 200 W and an operating frequency of 40 kHz.

6.7 Pestle and mortar, constructed of, or faced with, hard material which will not be abraded and thereby contaminate the sample.

NOTE Typical suitable materials include agate, tungsten carbide and silicon carbide.

6.8 Test sieve, of 212 µm nominal aperture, conforming to the requirements of ISO 565 and having a lid and receiver.

7 Sampling and preparation of the test sample

Prepare a representative sample of approximately 5 g to 10 g of the pitch by the method described in ISO 6257. Grind the sample with the pestle and mortar (6.7) until all the pitch passes through the test sieve (6.8).

8 Preparation of the test solutions

8.1 Test solution A — without added internal standard

Weigh approximately 1 g of the ground test sample (see clause 7) to the nearest 0,1 mg directly into a 10 ml volumetric flask (6.5).

Record the mass then add sufficient toluene (5.3) to fill the bulb of the flask without reaching the calibration mark, and loosely insert the stopper.

If the ultrasonic bath (6.6) has a heating facility capable of maintaining the contents at a temperature of 60 °C to 70 °C, place the flask in the bath and subject it to ultrasonic treatment at a temperature in this range for 20 min.

If the ultrasonic bath is not capable of maintaining its contents at 60 °C to 70 °C, heat the flask and its contents to 60 °C to 70 °C in a water bath for 5 min, then subject it to ultrasonic treatment for 5 min. Repeat the heating and ultrasonic treatment operations three more times, to give a total of 20 min ultrasonic treatment.

Remove the flask and allow it to cool to ambient temperature. Fill the flask with toluene up to the calibration mark, insert the stopper then shake the flask vigorously by hand for approximately 20 s. Allow the flask and its contents to remain undisturbed for a minimum of 1 h and preferably overnight to allow the suspended solid matter to settle before analysis.

Keep the solution out of direct sunlight or strong daylight, and at a temperature between 15 °C and 30 °C until required. Perform the analysis within 48 h of preparing the solution.

NOTE The settling period is intended to reduce the amount of insoluble material which is subsequently drawn with the solution into the syringe (6.4) and injected into the gas chromatograph (6.1), and thus to limit fouling of the injection port or column with involatile deposits which would otherwise degrade the performance of the system. Provided that care is taken to prevent any loss of the solution or its volatile components, the settling process may be shortened by centrifuging a suitably-sized aliquot portion, or by filtering through a suitable filter which does not interact with the solution.

8.2 Test solution B — with added internal standard

Weigh approximately 0,01 g of the dibenzothiophene (5.1) to the nearest 0,1 mg directly into a 10 ml volumetric flask (6.5) then prepare the solution as described in 8.1. Record the masses of dibenzothiophene and pitch taken.

9 Preparation of the calibrant solution — solution C

Weigh 0,1 g ± 0,001 g dibenzothiophene (5.1) and 0,001 g of each of the calibrant compounds (5.2) to the nearest 0,1 mg directly into a 100 ml volumetric flask (6.5); record the masses, then add sufficient toluene (5.3) to fill the bulb of the flask but remain below the calibration mark.

Place the flask in the ultrasonic bath (6.6) and subject it to ultrasonic treatment until all the solids have dissolved. Allow the flask to cool to ambient temperature then add toluene to bring the solution up to the calibration mark. Shake the flask to mix the solution.

Keep the solution out of direct sunlight or strong daylight and store it in the dark and at a temperature between 15 °C and 30 °C, until required. Discard the solution after one month and prepare a fresh solution.

10 Selection of chromatographic conditions

Set the operating parameters for the gas chromatograph (6.1), the capillary column (6.3) and the electronic integrator (6.2) for optimum performance in the following analysis, according to the manufacturer's instructions. Take care if the electronic integrator has a 'minimum area' facility which enables it to ignore small peaks, and ensure that this is set to the lowest value consistent with satisfactory operation.

Set the electronic integrator to ignore the toluene solvent peak and collect data only for the subsequent peaks.

Set the initial temperature, rate of temperature rise and final temperature of the gas chromatograph to values which give the most-nearly rectilinear relationship between the retention times of the components of solution C (see clause 9) and their atmospheric pressure boiling points. If the optimum temperature conditions for the capillary column (6.3) being used are not already known, start with the initial column temperature set at 60 °C, the rate of temperature rise to 5 K/min and the final temperature to 300 °C.

Make trial injections of solution C (see clause 9) using the selected temperature programme to determine the most convenient injection volume which gives large, well-defined symmetrical peaks without appreciable fronting or tailing, or departure from linearity of the quantitative response of the chromatograph detector or the electronic integrator.

The peak performance may be poor because the concentration of solution C is too high. In this case, rather than reduce the injection volume considerably below 1 µl, reduce the concentrations of all the solutions, for instance by dilution, and keep injection volumes to at least 1 µl. Reduce the concentration by increasing the solution volumes rather than by reducing the solute masses.

11 Calibration

11.1 Determination of the mean response factor

Inject solution C (see clause 9) using the temperature programme and injection volume selected in accordance with clause 10 to produce chromatogram C. Use the printed peak area values from the electronic integrator for the components of solution C to calculate the average response factor, R_f, for the calibrant compounds (5.2) with respect to the dibenzothiophene (5.1) from the equation:

$$R_\mathrm{f} = \frac{A_{\mathrm{d,C}} \times m_{\mathrm{tot,C}}}{m_{\mathrm{d,C}} \times A_{\mathrm{tot,C}}} \qquad (1)$$

where

$A_{d,C}$ is the area, in the units used by the electronic integrator, of the dibenzothiophene (5.1) peak;

$A_{tot,C}$ is the total sum of areas, in the units used by the electronic integrator, of the peaks for the calibrant compounds (5.2);

$m_{tot,C}$ is the total sum of the masses, in grams, of the calibrant compounds (5.2) in solution C (see clause 9);

$m_{d,C}$ is the mass, in grams, of the dibenzothiophene (5.1) in solution C (see clause 9).

11.2 Determination of the retention-time/boiling-point relationship

Calculate the relationship between the chromatographic retention times and the corresponding atmospheric pressure boiling points (see annex A) of the calibrant compounds (5.2) for chromatogram C by linear regression.

The use of a computer or pre-programmed calculator is recommended for performing the regression calculation. Where these are not available refer to a standard statistical textbook for the appropriate method.

12 Determination

Inject test solution A (8.1) and test solution B (8.2) using the temperature programme and injection volume selected in accordance with clause 10 to give respectively chromatogram A and chromatogram B.

13 Calculation and expression of results

13.1 Correction of the internal standard peak area

Identify the peaks in chromatogram A (see clause 12) for dibenzothiophene and phenanthrene by their retention times and calculate the ratio, K_A, of their respective areas from the equation:

$$K_A = \frac{A_{d,A}}{A_{p,A}} \qquad (2)$$

where

$A_{d,A}$ is the area, in the units used by the electronic integrator, of the dibenzothiophene peak in chromatogram A;

$A_{p,A}$ is the area, in the units used by the electronic integrator, of the phenanthrene peak in chromatogram A.

Identify the peaks in chromatogram B (see clause 12) for dibenzothiophene and phenanthrene by their retention times. Calculate the contribution, $A_{d,0}$, to the area of the dibenzothiophene peak, which resulted from the presence of dibenzothiophene in the original pitch sample from the equation:

$$A_{d,0} = K_A A_{p,B} \qquad (3)$$

where

$A_{p,B}$ is the area, in the units used by the electronic integrator, of the phenanthrene peak in chromatogram B.

Calculate the contribution, $A'_{\mathrm{d,B}}$, to the area of the dibenzothiophene peak in chromatogram B, which resulted from the addition of dibenzothiophene as an internal standard from the equation:

$$A'_{\mathrm{d,B}} = A_{\mathrm{d,B}} - A_{\mathrm{d,0}} \tag{4}$$

where

$A_{\mathrm{d,B}}$ is the area, in the units used by the electronic integrator, of the dibenzothiophene peak in chromatogram B.

13.2 Calculation of component masses and cumulative mass totals

Convert each of the tabulated peak areas of chromatogram B up to and including the peak for pyrene, but excluding dibenzothiophene, to the corresponding percentages by mass in the original pitch sample by multiplying them by the factor F given by the equation:

$$F = \frac{100 \times m_{\mathrm{d,B}} \times R_{\mathrm{f}}}{A'_{\mathrm{d,B}} \times m_{\mathrm{pitch}}} \tag{5}$$

where

$m_{\mathrm{d,B}}$ is the mass, in grams, of dibenzothiophene added to test solution B (see 8.2);

R_{f} is the mean response factor of the calibrant compounds calculated in 11.1;

$A'_{\mathrm{d,B}}$ is the contribution of the dibenzothiophene internal standard in chromatogram B calculated in 13.1, in the units used by the electronic integrator;

m_{pitch} is the mass, in grams, of pitch in test solution B (see 8.2).

Calculate the percentage by mass, $w_{\mathrm{d,pitch}}$, of dibenzothiophene present in the original pitch sample using the following equation:

$$w_{\mathrm{d,pitch}} = \frac{100 \times A_{\mathrm{d,0}} \times m_{\mathrm{d,B}}}{A'_{\mathrm{d,B}} \times m_{\mathrm{p,B}}} \tag{6}$$

Include the result at the appropriate point in the table of percentages by mass.

Transform the resulting table of percentages by mass into a table of cumulative percentages by mass by adding the value for each component to the total of all the previous values.

13.3 Calculation of corrected retention times and equivalent boiling points

Calculate the ratio, K_T, of the retention times of the dibenzothiophene peak in chromatograms C and B using the equation:

$$K_T = \frac{T_{\mathrm{d,C}}}{T_{\mathrm{d,B}}} \tag{7}$$

where

$T_{\mathrm{d,C}}$ is the retention time, in minutes, of the dibenzothiophene peak in chromatogram C;

$T_{\mathrm{d,B}}$ is the retention time, in minutes, of the dibenzothiophene peak in chromatogram B.

Multiply the tabulated retention times of each of the peaks in chromatogram B by K_T to give a table of corrected retention times. Convert each of these retention times to the equivalent boiling point at atmospheric pressure using the equation:

$$B_i = aT_i + b \qquad (8)$$

where

B_i is the equivalent boiling point, in degrees Celsius, at atmospheric pressure of the component producing the i-th peak;

T_i is the retention time, in minutes, of the i-th peak in chromatogram B;

a is the gradient of the regression line calculated in 11.2;

b is the intercept of the regression line calculated in 11.2.

13.4 Calculation of the volatile matter content

Tabulate the cumulative percentages by mass (see 13.2) against the corresponding equivalent atmospheric pressure boiling points (see 13.3) in the form of a distillation table.

Locate the temperature results immediately below and immediately above 360 °C, then from these and the corresponding cumulative percentages calculate the percentage distilled at 360 °C by linear interpolation. Record the result as the volatile matter content, expressed to two significant figures.

14 Precision

14.1 Repeatability

The results of duplicate determinations, carried out in the same laboratory by the same operator with the same apparatus but at different times on representative test portions taken from the test sample, should not differ by more than r, calculated from the equation:

$$r = 0{,}168 + 0{,}054\,\bar{x}$$

where $\bar{x}$ is the mean volatile matter content, in percentage by mass, expressed as the mean of duplicate tests carried out in a single laboratory.

14.2 Reproducibility

The means of the results of duplicate determinations carried out in each of two laboratories on representative test portions taken from the same sample after the last stage of sample preparation, should not differ by more than R calculated from the equation:

$$R = 0{,}125 + 0{,}071\,\bar{X}$$

where $\bar{X}$ is the average volatile matter content, in percentage by mass, expressed as the mean of four tests in two laboratories.