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Carbonaceous materials used in the production of aluminium - Pitch for electrodes - Part 13: Determination of C/H ratio in the quinoline-insoluble fraction

原铝生产用炭素材料 煤沥青 第13部分：喹啉不溶物中C/H原子比的测定

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2 Normative references

The following documents are indispensable for the application of this document. For dated references only the edition cited applies; for undated references the latest edition, including any amendments, applies.

The documents listed are ISO 565, Test sieves - Metal wire cloth, perforated metal plate and electroformed sheet - Nominal sizes of openings; ISO 4788, Laboratory glassware - Graduated measuring cylinders; and ISO 6257, Carbonaceous materials used in the production of aluminium - Pitch for electrodes - Sampling.

3 Principle of the method

Crushed and finely ground coal tar pitch is dissolved in hot quinoline and the quinoline insolubles are obtained by pressure filtration through a membrane. On the membrane the insolubles are washed first with hot quinoline, then with hot toluene, and finally dried.

The dried material is burned completely in a stream of oxygen; the carbon dioxide and the water produced by the combustion are separated and weighed to establish the carbon and the hydrogen content of the quinoline insolubles, and the C/H atomic ratio of the insolubles is calculated from those contents and from the relative atomic masses.

4 Separation of the quinoline insolubles used for the analysis

4.1 Reagents. Warning: refer to the safety and health data supplied by the reagent supplier for the precautions to be taken with quinoline and toluene. 4.1.1 Quinoline: purity not less than 97 %, freshly distilled, boiling point 235 °C to 237 °C at 0.101 3 MPa. After distillation the quinoline is kept in a stoppered dark glass bottle at a temperature between 5 °C and room temperature and used within two weeks; beyond that period it shall not be used, or shall be redistilled. 4.1.2 Toluene. 4.1.3 Nitrogen or another inert gas: supplied through a two-stage reducing valve, the outlet pressure not exceeding 0.45 MPa.

4.2 Apparatus. Warning: before the pressure filtration unit is used, make sure that suitable safety equipment is fitted and that the unit has been tested and meets the relevant safety and health regulations. 4.2.1 Temperature-controlled hotplate: able to hold the liquid in the beaker at 70 °C to 80 °C. 4.2.2 Pressure filtration unit: fitted with a filter disc 47 mm in diameter, designed for safe operation above 120 °C and above 1 MPa of gas pressure. Figure 1 shows a typical unit; its key names 1, top cover; 2, locating rod; 3, silicone O ring; 4, pressure hose connector; 5, silicone O ring; 6, perforated support disc; 7, wire mesh support; 8, outlet connector. 4.2.3 Membrane filter disc: polytetrafluoroethylene (PTFE), 47 mm in diameter, with pores of nominal size 0.2 micrometre. 4.2.4 Hand-held electric hot air blower: general laboratory type, rated power 500 W, air outlet temperature about 300 °C. 4.2.5 Test sieve: nominal size 212 micrometre, complying with ISO 565, with lid and receiver. 4.2.6 Watch glass: about 70 mm in diameter, dried for 1 h at 105 °C to 110 °C and cooled in a desiccator. 4.2.7 Measuring cylinder: borosilicate glass, capacity 50 mL, with a lip, complying with ISO 4788.

4.3 Sampling and sample preparation. About 10 g of representative pitch sample is taken by the method of ISO 6257 and ground in a mortar until it all passes the test sieve of 4.2.5.

4.4.1 A 100 mL borosilicate glass beaker is weighed to 0.1 mg, about 1 g of the sample of 4.3 is put in and the beaker is weighed again to 0.1 mg. Using the measuring cylinder of 4.2.7, 25 mL of the quinoline of 4.1.1 is measured into the beaker, the coarse particles are crushed with a glass rod, the solution is stirred, the beaker is covered with the watch glass and placed on the hotplate of 4.2.1, and the mixture is leached for 20 min at 70 °C to 80 °C, the beaker being stirred about every 5 min. While the leaching proceeds, the filter support and the vessel that receives the filtrate in the pressure filtration unit of 4.2.2, shown in Figure 1, are heated to near 100 °C in an oven or with the hot air blower of 4.2.4. When leaching is nearly complete, the membrane filter disc of 4.2.3 is weighed to 0.1 mg, placed on the heated filter support, and the filtration unit is assembled so that it is gas tight. A note adds that the membrane disc curls when it is placed on the heated support, and that an effective way of dealing with this is to put an O ring on the disc each time before placing it on the support, which keeps the disc flat during the rest of the operation.

4.4.2 The measuring cylinder is placed under the outlet of the pressure filtration unit. To keep liquid from being sprayed into the gas stream, a small glass funnel is used to transfer the leached pitch and quinoline mixture from the beaker to the liquid vessel of the unit. The

unit is closed, inert gas is fed in and the gas pressure is raised step by step until the liquid passes the filter and runs into the graduated receiver. A note states that material generally begins to filter through when the pressure reaches 0.12 MPa to 0.14 MPa. The lowest pressure that gives a satisfactory steady flow rate is used; the filtration rate is judged from the volume of filtrate in the receiver, and if filtration is slow the unfiltered liquid is held at 70 °C to 80 °C with the hot air blower. A further note states that the filtration rate is closely related to the nature of the pitch tested: a lightly heat-polymerised or non-heat-polymerised electrode binder pitch filters completely in 1 min at a pressure of 0.13 MPa, whereas a deeply heat-treated pitch filters very slowly and usually takes 1 h; in that case holding the temperature of the filtration unit is the decisive point, releasing and re-applying pressure from time to time is also helpful, and applying more than 0.2 MPa of gas pressure brings no marked improvement in the filtration rate.

4.4.3 When the quinoline solution has been filtered, the pressure is released and the beaker is washed with about 5 mL of quinoline at 70 °C to 80 °C, the washings being transferred to the filtration unit through the glass funnel. The filter is closed and the pressure is raised slowly until filtration starts; this usually calls for about 0.1 MPa, the pressure being adjusted to give a satisfactory filtration rate. The washing of the beaker and of the undissolved material on the filter is then repeated nine more times, each time with about 5 mL of quinoline at 70 °C to 80 °C, until the colour of the wash liquid leaving the unit is almost as deep as that of the distilled quinoline of 4.1.1. If the washings are still deeply coloured, washing with equal volumes of hot quinoline is continued until the colour of the quinoline coming out no longer becomes lighter. The insoluble material on the filter is then washed successively with ten 5 mL portions of the toluene of 4.1.2 at 70 °C to 80 °C, the gas pressure being lowered to about 0.01 MPa to 0.02 MPa to control the filtration rate, so that the last washing takes 1 min to 2 min to filter.

4.4.4 The watch glass of 4.2.6 is weighed to 0.1 mg. The membrane filter disc is placed on the watch glass; where a good deal of quinoline insoluble matter has stuck to the O ring, the ring is placed on the watch glass as well. The watch glass and what it carries are put in an oven at 105 °C to 110 °C for 2 h, then taken out and cooled in a desiccator. Any quinoline insolubles sticking to the O ring are brushed gently onto the watch glass. The watch glass, the membrane filter disc and the quinoline insolubles are weighed to 0.1 mg. The membrane disc is put into a test tube with tweezers, with the watch glass underneath, and the tweezers are flicked hard so that as much of the insoluble matter as possible falls off. The membrane disc is then laid flat on a clean smooth sheet of paper and all the residue on it is carefully brushed off. The quinoline insolubles obtained are transferred to a clean small bottle of suitable size ready for the next stage of the analysis. A note adds that a No. 5 artist's brush is convenient for brushing the quinoline insolubles.

4.4.5 Where the amount of quinoline insolubles collected is not enough for the analysis that follows, the extraction from the pitch is repeated, the amounts of pitch and of quinoline used in a single separation being increased in the same proportion to 5 g and 125 mL. Where the

quinoline insolubles are still not enough after that increase, the whole extraction is repeated with a further 5 g of sample until the requirement is met.

4.5 Calculation and expression of the result. The content of quinoline insolubles, wqi, is expressed as a mass fraction and calculated by formula (1). The printed equation is not reproduced here; its legend is: m1, the total mass of the watch glass, the membrane filter disc and the extracted quinoline insolubles, in grams; m2, the mass of the watch glass, in grams; m3, the mass of the membrane filter disc, in grams; m4, the mass of the beaker holding the pitch sample, in grams; m5, the mass of the empty beaker, in grams. The calculated result is kept to two significant figures. A note states that this result cannot be taken as the result of a determination of the quinoline insoluble content of the pitch, which is to be determined according to GB/T 26930.4.

5 Analysis of the carbon and hydrogen content of the quinoline insolubles

5.1 Reagents. Warning: refer to the safety and health data supplied by the reagent supplier for the precautions to be taken with the two reagents magnesium perchlorate and sodium hydroxide on a synthetic silicate carrier. 5.1.1 Magnesium perchlorate: anhydrous, analytical grade, particle size 0.7 mm to 1.2 mm. 5.1.2 Sodium hydroxide on a synthetic silicate carrier: analytical grade, particle size 1.5 mm to 3.0 mm. 5.1.3 Woven silver wire mesh: wire diameter about 0.3 mm, aperture about 0.8 mm. 5.1.4 Silver metal wire: for microanalysis, typical wire diameter about 0.05 mm. 5.1.5 Quartz fibre. 5.1.6 Oxygen: purity greater than 99.5 %, supplied through a two-stage reducing valve and a needle valve, the flow rate being held at not more than 500 mL/min.

5.2.1 Carbon and hydrogen analyser: made up of the items of 5.2.2 to 5.2.8. 5.2.2 Combustion boat: porcelain, about 60 mm long, about 10 mm wide and about 8 mm high, with a small hole at one end so that it can be attached to the transport mechanism of 5.2.6. 5.2.3 Combustion tube: made of dense alumina, 900 mm long, 23 mm outside diameter and 18 mm inside diameter, usable up to 1 400 °C. 5.2.4 Combustion furnace: electrically heated, able to heat a zone of the combustion tube of 5.2.3 at least 100 mm long, with a maximum temperature of 1 400 °C, and connected to a temperature control device. 5.2.5 Auxiliary furnace: electrically heated, able to hold a zone of the combustion tube at least 80 mm long within 730 °C +/- 5 °C; it is placed behind the combustion furnace and coaxial with it.

5.2.6 Transport mechanism, shown in Figure 2: able to carry the combustion boat holding the quinoline insolubles at a speed of 20 mm/min without any other mechanical device being connected from outside, and to bring the boat finally to the centre of the heated zone of the combustion furnace. A typical transport mechanism has a cylindrical soft iron rotor placed inside the combustion tube and connected to the small hole of the combustion boat by an insulated metal hook; a variable-speed motor drives a cylindrical solenoid that