ICS 71.100.10
CCS Q 52



# NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

# GB/T 26930.10-2014

# Carbonaceous materials used in the production of aluminium - Pitch for electrodes - Part 10: Determination of sulfur content by an instrumental method

原铝生产用炭素材料 煤沥青 第10部分：仪器法测定硫含量

**Issued on: July 24, 2014** **Implemented on: April 1, 2015**

**Issued by: State Administration for Market Regulation;**
**Standardization Administration of the PRC**

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## 1 Scope

This part of GB/T 26930 lays down the method for determining the sulfur content of coal tar pitch used in the production of primary aluminium.

It applies to the determination of sulfur in coal tar pitch over the range 0.1 % to 4.0 %.

## 2 Normative references

The documents listed below cannot be dispensed with for the application of this part. For dated references only the edition corresponding to that date, including any amendments, applies; for undated references the latest edition applies.

ISO 565 Test sieves - Metal wire cloth, perforated metal plate and electroformed sheet - Nominal sizes of openings.

ISO 3696 Water for analytical laboratory use - Specification and test methods.

ISO 4793 Laboratory sintered (fritted) filters - Porosity grading, classification and designation.

ISO 6257 Carbonaceous materials used in the production of aluminium - Pitch for electrodes - Sampling.

## 3 Principle of the method

A test portion of known mass is burnt at 1 350 °C in an atmosphere of oxygen. The oxides of sulfur produced are absorbed in a neutral hydrogen peroxide solution and determined

volumetrically.

The error caused by the chlorine content of the test portion has to be allowed for, and aluminium oxide is added to prevent sulfur being retained in the ash.

## 4 Reagents

Unless otherwise stated, analytical grade reagents and water complying with grade 3 of ISO 3696 are used.

4.1 Sodium borate solution, c(1/2 Na2B4O7 10H2O) = 0.025 mol/L.

4.2 Sulfuric acid solution, c(1/2 H2SO4) = 0.025 mol/L.

4.3 Hydrogen peroxide solution: 3 % hydrogen peroxide with 97 % (volume fraction) of water.

4.4 Green indicator, made up of the two solutions a) and b), which are mixed before use: a) 0.125 g of methyl red dissolved in 100 mL of 95 % (volume fraction) ethanol; b) 0.083 g of methyl blue dissolved in 100 mL of 95 % (volume fraction) ethanol. Store in a dark glass bottle.

4.5 Mercury(II) oxycyanide [3Hg(CN)2 HgO] solution: about 100 mL of saturated mercury(II) oxycyanide is stirred, filtered, and then neutralised with the sulfuric acid solution (4.2) using the green indicator. The solution is stored in a dark glass bottle and kept for not more than four days. Warning: this compound and its solutions are strongly toxic and are to be handled with particular care.

4.6 Aluminium oxide: carefully sieved so that the particle size is about 0.1 mm.

4.7 Oxygen.

4.8 Sodium hydroxide: placed on a non-reacting support, preferably of the self-indicating type graded from 1.7 mm to 1.2 mm.

## 5 Apparatus

5.1 Combustion furnace and absorption device, as shown in Figure 1, made up of the parts listed below.

5.1.1 Furnace: electrically heated, able to take a tube of 28.5 mm outside diameter, with a heated band longer than 125 mm and a heating temperature in the central zone reaching 1 350 °C. The temperature distribution in the furnace chamber is similar to the curve of Figure 2.

5.1.2 Combustion tube: inside diameter 22 mm, outside diameter 28.5 mm, length 0.65 m, made of refractory alumina ceramic that does not vitrify at 1 400 °C.

5.1.3 Combustion boat: unglazed ceramic free of iron, 70 mm long, 12.5 mm wide and 10 mm deep, showing no change of colour or of mass after 3 h of heating at 1 350 °C in an oxygen atmosphere.

5.1.4 Quartz push rod: a sealed tube or quartz rod of 6 mm diameter and about 450 mm length, one end being a flat circular face of 12 mm diameter, used to push the combustion boat into the furnace. The rod is to slide easily in the adapter tube. The other end is sealed with a rubber sleeve, and the rod is graduated in millimetres so that the depth reached by the boat inside the combustion tube can be read.

5.1.5 Hook: a nickel-chromium wire of a given length, hooked at one end, used to move the burnt boat out of the furnace onto a heat-resistant mat.

5.1.6 Flow meter: able to measure an oxygen flow up to 300 mL/min.

5.1.7 Pressure gauge: measures the back pressure of the system, normally between 0.5 kPa and 0.7 kPa.

5.1.8 Insulating stopper: made of acrylonitrile-butadiene or chloroprene rubber.

5.1.9 Quartz adapter tube: translucent quartz tube of 10 mm outside diameter and about 250 mm length, one end of which is inserted into the furnace chamber and has an outside diameter of 20 mm.

5.1.10 Purification device: the incoming gas passes through a sodium hydroxide purification tower which removes any sulfur oxide from the oxygen stream, the sodium hydroxide being held on the support described above.

5.1.11 Absorption vessel: a wash bottle fitted with a multi-hole sintered disc of grade P40 to ISO 4793, holding 100 mL of liquid, with a 90 mm liquid seal.

5.1.12 Pressure stabilizer: a bottle holding the mercury compound, fitted with an inlet and an outlet tube and with a tube that can be raised and lowered to adjust the suction of the system.

5.1.13 Vacuum pump, or another suitable pump.

## 6 Connection of the apparatus

The combustion tube is inserted into the furnace so that about 100 mm of its outlet end projects beyond the furnace. The insulating stopper carrying the quartz adapter tube is fitted at that end and the adapter is adjusted; the rubber stopper carrying the quartz push rod is fitted at the inlet end of the combustion tube, at a depth of about 150 mm, and the oxygen coming from the purification device is connected to the T-piece.

## 7 Sampling and sample preparation

7.1 Sampling is carried out in accordance with ISO 6257.

7.2 The test sample is prepared before the determination. When the pitch is on the hard side, the crushed sample is passed through a 212 micrometre sieve whose specification complies with ISO 565. When the pitch is too soft to be crushed, the sample is melted and mixed in a covered vessel, the melting temperature being kept at not more than 150 °C and the melting time at not more than 10 min; the test portion is then taken from the molten sample.

## 8 Determination procedure

The furnace (5.1.1) is heated to 1 350 °C and oxygen (4.7) is passed through the combustion tube (5.1.2). About 0.5 g of the test sample (7.2) is weighed to the nearest 0.1 mg, spread evenly in the combustion boat (5.1.3) and covered with 0.5 g of aluminium oxide (4.6). 100 mL of the hydrogen peroxide solution (4.3) is placed in the absorption vessel (5.1.11), the depth of the liquid seal being adjusted to the stated value. A slight suction is applied to the oxygen in the combustion tube through the vacuum pump (5.1.13) and the pressure stabilizer (5.1.12), and the oxygen flow shown by the flow meter (5.1.6) at the inlet of the combustion tube is 300 mL/min.

The rubber stopper carrying the push rod is removed, the boat loaded with the sample is pushed into the combustion tube to the position 240 mm from the zone of highest temperature, the push rod is fully withdrawn, the stopper is refitted and the oxygen flow is kept at 300 mL/min. Over the following 12 min the boat is pushed forward 20 mm every minute; to prevent the rod from distorting, the rod is withdrawn each time a push has been completed. The boat is finally left for 4 min in the zone of highest temperature. As an alternative, the boat may be advanced continuously by a mechanical device following a set schedule. The boat is then moved onto a heat-resistant mat with the hook (5.1.5).

The quartz adapter tube is washed and the washings are collected in a 250 mL flask. The solution of the absorption device is poured into the flask, the device is rinsed and the rinsings are also added to the flask. Two to three drops of the green indicator (4.4) are added and the solution is titrated with the sodium borate solution (4.1) until it turns grey. 10 mL of the mercury(II) oxycyanide solution (4.5) is added, which is enough for a chlorine content in the pitch of up to 0.5 %, and the solution is then titrated with the sulfuric acid solution (4.2) until it turns grey.

Note 1: if the sample burns too fast and the gas is not completely absorbed in the wash bottle, the boat should be pushed forward 10 mm every minute over 24 min.

Note 2: the total volume of liquid should not exceed 150 mL.

Note 3: a white background is strongly recommended for the titration.