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Chemical analysis of graphite materials

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Chemical analysis of graphite materials

1 Scope This Japanese Industrial Standard specifies the chemical analysis of graphite material (hereafter referred to as "material").

Remarks : The normative references to this Standard are shown in Attached Table 1.

2 Analysis items Analysis items specified in this Standard shall be as follows :

- (1) Boron
- (2) Ash content

3 Common apparatus

3.1 Balance The weighing capacity of the balance to be used shall be not less than 100 g and its reciprocal sensibility shall be 0.1 mg.

3.2 Glass devices and ceramic wares for chemical analysis The glass devices and ceramic wares for chemical analysis used in this Standard, unless especially specified, shall conform to the following standards :

- (1) JIS R 1301
- (2) JIS R 1302
- (3) JIS R 1303
- (4) JIS R 1305
- (5) JIS R 1306
- (6) JIS R 1307
- (7) JIS R 3503
- (8) JIS R 3505

3.3 Thermometer For the thermometer, a mercury-in-glass thermometer of 0 °C to 150 °C in range, shall be used.

3.4 Dryer For the dryer, an electric thermostat with automatic temperature regulator capable of being kept at a temperature of 105 °C to 110 °C, shall be used.

3.5 Vessel of distilled water For the vessel of distilled water, a polyethylene vessel shall be used.

4 Rounding off of numerical values Measured and calculated values shall be rounded off according to JIS Z 8401.

5 Analysis method of boron

5.1 Summary The analysis method of boron contained in material at the rate of about 0.01 ppm to 2 ppm is specified therein. The determination method of boron shall be classified into the following three methods; (1) colorimetric analysis method, (2) incineration carrier distillation emission spectrochemical analysis method, (3) concretion direct emission spectrochemical analysis method, and any of them may be used.

5.2 Sampling method for analysis The sampling method for analysis shall be as follows :

- (1) A sample piece shall be sampled from the material. The sampling method shall be subjected to the agreement between the parties concerned.
- (2) A necessary amount of powdery sample shall, as a rule, be cut off from the sample piece with giving attention to the following items:

Further, the sample shall be put into a clean vessel to be stored.

- (a) A necessary amount of powdery sample shall be obtained from respective parts of sample piece.
- (b) In the case of taking the powdery sample by using a drill, the drill of the hardness of G2 specified in **JIS H 5501** or that equal or superior thereto in hardness shall be used, cleaned with alcohol or the like before use and further sufficiently cleaned by preliminarily drilling the material.
- (c) The powdery sample shall be taken from clean positions having no fear of pollution due to dust or the like.

5.3 Expression of analysis results The analysis results shall be expressed by ppm and the numerical value of ppm shall be rounded off to two places of significant figures. However, in the case where the significant figure of two places extends to three places of decimals, the numerical value of the three places of decimals and under shall be rounded off to two places of decimals.

5.4 Colorimetric analysis method

5.4.1 Summary A sample is incinerated together with calcium hydroxide and the boron in sample is captured with calcium oxide. This incinerated substance is processed with ethanol distillation under sulfuric acid acidic state and boron is separated by distillation as methyl borate. It is absorbed into lime water and evaporated to dryness together with curcumin reagent. The generated red compound is extracted with ethanol and the absorbancy of that red solution is measured.

5.4.2 Incineration treatment A powdery sample is taken⁽²⁾ into the platinum vessel⁽¹⁾ the contents of which are confirmed not to be contaminated with boron by preliminarily carrying out a blank test so that boron becomes about 0.5 µg to 2 µg, added with 3 % calcium hydroxide⁽³⁾ suspension⁽⁴⁾ at a rate of 1 ml per 1 g of the sample, sufficiently permeated by mixing, dried and the dry sample is exfoliated⁽⁵⁾ from the vessel with a platinum bar. Thereafter, it is put into an electric furnace⁽⁶⁾ and clean oxygen⁽⁷⁾ is let to pass therethrough at (880 ±20) °C. It is completely incinerated.

Notes (1) A platinum crucible or a platinum boat is used. Those vessels shall be clean.

Because the platinum vessel ignited together with a great amount of boron is contaminated with boron, it is occasionally not cleaned even by boil cleaning generally carried out with concentrated hydrochloric acid, or otherwise by fusion cleaning with potassium pyrosulfate. When the platinum vessel contaminated with boron is ignited (about 1 200 °C) together with, for example, refined calcium hydroxide, boron is observed to be increased in the calcium oxide after ignition by comparing it to that before ignition. This increase of boron by ignition is gradually decreased by repeating ignition by exchanging new calcium oxide and becomes not to be observed at last. The platinum vessel having reached to this state is here called clean.

- (2) 10 g for the sample of not more than 0.1 ppm in boron content, 2 g to 5 g for the sample of 0.1 ppm to 1 ppm, and 1 g shall be sampled for the sample of not less than 1 ppm.
- (3) Calcium hydroxide shall be refined to be used.

An example of refining method Dissolve 11 g of anhydrous calcium chloride with about 60 ml of methanol specified in **JIS K 8891**, blow in hydrogen chloride gas and sufficiently make it acid. Remove boron by processing it by methanol distillation with a boron distillation apparatus and allow it to be solution A. Separately dissolve 13 g of oxalic acid specified in **JIS K 8519** with about 60 ml of methanol specified in **JIS K 8891**, sufficiently make it acid by blowing in hydrogen chloride gas, remove boron in the same way as that for solution A and allow it to be solution B. Mix the solutions A and B, blow in ammonia vapor, make the precipitate of calcium oxalate by neutralizing acid, further stand it on a water bath for all day and grow the precipitate. Wash this precipitate by filtration with a Buchner funnel by decantation and dry it.

Transfer the precipitate onto a quartz glass dish, make it calcium oxide by igniting it (about 1 000 °C) in an electric furnace, react it with water and obtain refined calcium hydroxide.

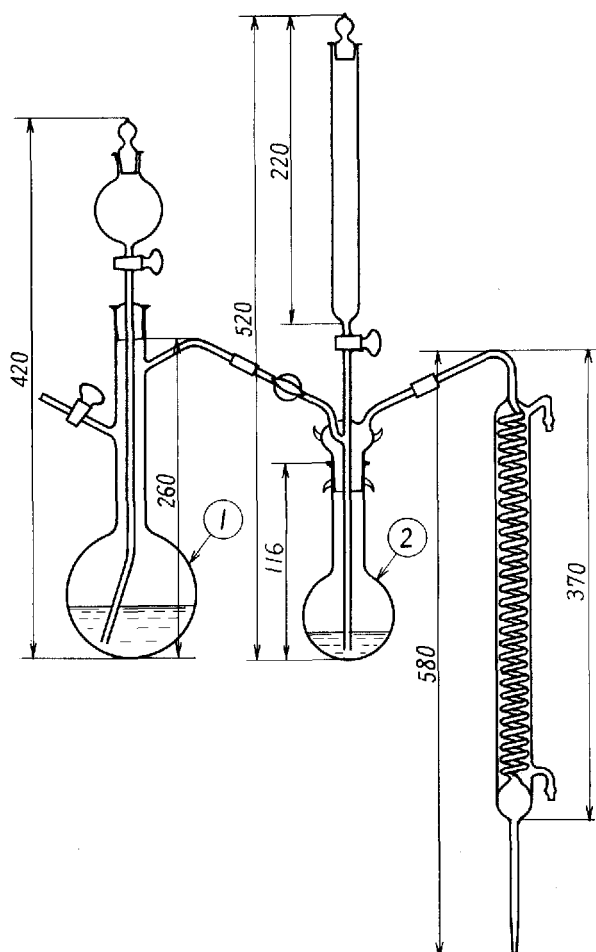
- (4) The suspension shall be stored in the vessel without contamination with boron, for example, a polyethylene vessel.
- (5) Empty the contents of the platinum vessel after drying onto a clean cartridge paper, rub off the sample adhered to the inside of platinum vessel as completely as possible by using a platinum bar, wash the platinum vessel with dilute hydrochloric acid, wash it with water, dry it and transfer the dry sample transferred onto the cartridge paper into the platinum vessel again.
- (6) A quartz glass tubular furnace or a muffle furnace is used. In the case of the muffle furnace, the inside wall of furnace is covered with quartz glass plate, and quartz glass plate is laid on its bottom.
- (7) Wash the oxygen with the mixed solution of chromic acid and sulfuric acid, then neutralize it by washing it with alkali solution, pass it through drying agent and clean it by passing it through the dedusting apparatus of glass wool or the like at last.

5.4.3 Distillation Completely wash down⁽⁹⁾ the incinerated sample into the decomposition flask of distillation apparatus⁽⁸⁾ by using a small amount of methanol as washing agent, connect it to the decomposition apparatus, add 20 ml of the mixed solution⁽¹¹⁾ of sulfuric acid and methanol⁽¹⁰⁾ by pouring from the funnel tube of upper part of decomposition flask, heat both the decomposition flask and the methanol vapor generation flask on a water bath and take 10 ml of the fraction into the receiver preliminarily put with 10 ml calcium hydroxide saturated solution.

Notes ⁽⁸⁾ The distillation apparatus is made of quartz glass or boric acidless glass and its shape and size are referred to Fig. 1.

About 1 g of mannitol specified in **JIS K 8882** and phenolphthalein specified in **JIS K 8799** as indicator and the methanol solution added with about 1 g of potassium hydroxide specified in **JIS K 8574** to turn its red color are preliminarily put into the methanol vapor generation flask.

Unit : mm



- ① Methanol vapor generation flask of about 300 ml in capacity
- ② Decomposition flask of about 100 ml in capacity

Fig. 1 Boron distillation apparatus

- (9) In the case of the blank test after incineration treatment, calcium oxide becomes solid and is occasionally not dispersed with the mixed solution of sulfuric acid and methanol in the decomposition flask when distilled. To prevent that, it is preferable that powdery calcium hydroxide is formed by adding several drops of water into the platinum vessel and transferred to the decomposition flask.
- (10) 2.5 volumes of methyl specified in **JIS K 8891** is added with one volume of sulfuric acid specified in **JIS K 8951** in the polyethylene vessel while cooling them and mixed.
- (11) Before use, about 60 ml of the mixed solution is put into the decomposition flask and processed with methanol distillation. About 30 ml of the fraction is discarded and about 30 ml of residual refined solution is used.

5.4.4 Evaporation coloring Transfer the fraction collected in the receiver into a distillation vessel⁽¹²⁾, add 4 ml of curcumin reagent⁽¹³⁾, put it into the thermostat water bath regulated at 55 °C to 60 °C, evaporate it to dryness at a place where there is no direct rays of the sun, keep it at the same temperature for 2 h after evaporation to dryness and make the coloring perfect.

Do not stop the operation of evaporation coloring together with the following absorbancy measurement halfway. Complete the determination by continuous operation.

Notes (12) Though appliances having no fear that boron is eluted during operation (for example, platinum, quartz glass or porcelain made) are used, they shall be of the same shape and size.

- (13) 0.04 g of curcumin specified in **JIS K 8297** and 5 g of oxalic acid (guaranteed grade) specified in **JIS K 8519** are dissolved with 100 ml of ethanol (guaranteed grade) specified in **JIS K 8101** and refluxed by boiling for not less than 1 h. Thereafter, it is cooled and stored in a polyethylene vessel.

5.4.5 Absorbancy measurement The colored substance is completely eluted by dissolution by adding 25 ml of ethanol⁽¹⁴⁾ specified in **JIS K 8101** to the colored dry substance and this eluted solution is filtered with a filter paper of class 6 (11 cm in diameter) specified in **JIS P 3801**. The filtrate is put into an absorption vessel and the absorbancy is measured by using ethanol as reference solution at near 550 nm in wavelength. The amount of boron is obtained according to the working curve⁽¹⁵⁾ separately prepared. The ppm of boron is calculated according to the following formula from the amount of boron and the value of blank test⁽¹⁶⁾.

$$[B] = \frac{a - c}{s}$$

where, [B] : boron (ppm)

s : mass of sample (g)

a : detection amount of boron (μg)

c : blank test value (μg)

The determination is carried out twice at least and the boron is expressed by the mean value.

Notes ⁽¹⁴⁾ Ethanol of approx. grade 1 may be used.

- ⁽¹⁵⁾ Prepare several classes of boron standard solutions with known boron contents within a range of 0 μg to 2 μg in the reaction flasks of distillation apparatus, distill them, hereafter measure the absorbancies according to the operation in the body and obtain the relation between the absorbancy and the amount of boron on section paper to be the working curve. Dissolve 0.572 g of boric acid (guaranteed grade) specified in **JIS K 8863** with distilled water and dilute it to 1 000 ml for the boron standard solution. Separately take 100 ml of this solution and dilute it to 1 000 ml with distilled water to be the stock solution. Further dilute this stock solution 10 times to be the standard solution of 1 $\mu\text{g}/\text{ml}$.
- ⁽¹⁶⁾ The blank test is carried out by using no sample over all operations on and after the addition of 3 % calcium hydroxide suspension in the same operation as that in the case of sample analysis each time.

5.5 Incineration carrier distillation emission spectrochemical analysis method

5.5.1 Summary A sample is incinerated together with lanthanum oxide and the boron in sample is captured in lanthanum oxide. This incinerated substance is added with carrier (indium oxide) so that it becomes 2 % and sufficiently mixed. 100 mg of this substance is weighed out, packed into an electrode and emitted by excitation by direct current arc method. That spectrum is photographed with a spectrograph and the intensity of spectral line is measured to be determined.

5.5.2 Incineration treatment Take⁽¹⁸⁾ powdery sample so that boron becomes about 0.4 ppm to 5 ppm in lanthanum oxide⁽¹⁷⁾, put it into a platinum vessel⁽¹⁾, add lanthanum oxide thereto, sufficiently mix them with a platinum bar and permeate it with distilled water. Thereafter, dry it on a hot plate. After exfoliating⁽⁵⁾ the dry sample from the vessel with the platinum bar, put it into an electric furnace⁽⁶⁾ and completely incinerate it with passing clean oxygen specified in **JIS K 1101** at $(880 \pm 20)^\circ\text{C}$. After incineration, take it out from the electric furnace, immediately put it into a desiccator (drying agent: phosphorus pentaoxide) and cool it. Thereafter, sufficiently mix it in a mortar.

Notes ⁽¹⁷⁾ Lanthanum oxide is refined to be used. As example of the refining method thereof, the following methods exist.

Method of recrystallization After dissolving lanthanum oxide on the market with minimum known amount of nitric acid specified in **JIS K 8541**, neutralize two thirds amount of the used nitric acid with aqueous ammonia specified in **JIS K 8085**. If some precipitate is generated in that case, remove it by filtration. After diluting the obtained solution with distilled water so as to become 10 % nitric acid aqueous solution, concentrate it by evaporation until small crystals are generated on the surface of solution, spray a small amount of water onto its surface and stand it for all day. Separate the precipitated crystals from mother solution and wash it with distilled water. Add a small amount of distilled water to the obtained lanthanum ammonium double salt $[\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}]$ and heat them. After dissolution,

recrystallize it by rapid cooling. After carrying out recrystallization 4 times to 5 times, take a portion thereof, make it oxide, add indium oxide so as to become 2 % to lanthanum oxide, emit it and photograph it. If the spectral line of boron is intensely detected, further repeat recrystallization. Put the refined double salt into the platinum vessel, heat it with direct flame of Bunsen burner and expel nitrogen oxide gas. Thereafter, put it into the electric furnace and heat it at $(880 \pm 20)^\circ\text{C}$ for about 3 h. After heating, take it out, put it into a desiccator and cool it. Thereafter, sufficiently grind it down in a mortar and mix it. Put the refined lanthanum oxide into a polyethylene bottle with a cover and store it in the desiccator.

Method by distillation Dissolve the lanthanum oxide on the market with 12 mol/l guaranteed grade hydrochloric acid specified in **JIS K 8180** in a quartz glass vessel or a boric-acidless glass vessel and concentrate it by evaporation to hydrous lanthanum chloride ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$). Grind the hydrous lanthanum chloride, add the same amount of ammonium chloride specified in **JIS K 8116** refined by sublimation thereto, sufficiently mix them, put it into a quartz glass boat and remove water by heating it at about 200°C . Heat it at 350°C midway and after. Obtain anhydrous lanthanum chloride according to above-mentioned operation. Store it in a desiccator.

Dissolve about 16.6 g of anhydrous lanthanum chloride with about 100 ml of methanol, blow in hydrogen chloride gas and sufficiently make it acid. Distill it with the boron distillation apparatus used for colorimetric analysis, remove boron and allow it to be solution A. Allow the initial distilled amount to be about 30 ml and discard it.

Separately dissolve 20 g of oxalic acid with about 100 ml of methanol, blow in hydrogen chloride gas and sufficiently make it acid. Distill it in the same way as that for solution A, remove boron and allow it to be solution B.

Mix solutions A and B, blow in ammonia vapor and generate the precipitate of lanthanum oxalate by neutralizing acid. Wash it by filtration with Buchner funnel and dry it. Then, put it into a quartz glass dish, heat it at about $1\,000^\circ\text{C}$ in an electric furnace and allow it to be lanthanum oxide. Store it in a desiccator.

- (18) 40 g for the sample of not more than 0.05 ppm in boron content per 1 g of lanthanum oxide, 20 g for the sample of 0.05 ppm to 0.1 ppm, 2 g to 10 g for the sample of 0.1 ppm to 1 ppm and 1 g is sampled for the sample of not less than 1 ppm. However, in the case of not less than 10 g, cumulative incineration is preferable.

5.5.3 Treatment of incinerated sample Weigh out the incinerated sample⁽¹⁹⁾, add indium oxide⁽²⁰⁾ as carrier so as to become 2 % to the incinerated sample, sufficiently mix them and divide it into each 100 mg. Work⁽²¹⁾ a graphite bar for spectrochemical analysis to be the electrode packed with the sample, fill 100 mg of incinerated sample thereinto, push it as tightly as possible and allow a pinhole to be hollowed in its center⁽²²⁾. Allow it to be the bottom electrode. Prepare three pieces of such bottom electrodes per one sample.