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**General rules for determination of sulfur
in metallic materials**

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by The Japan Society for Analytical Chemistry (JSAC)/ Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14.

Consequently **JIS Z 2616** : 2006 is replaced with this Standard.

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General rules for determination of sulfur in metallic materials

1 Scope

This Japanese Industrial Standard specifies the general rules that are commonly applied to the determination of sulfur in metallic materials. However, the requirements of the wet type decomposition method shall be as specified in each individual standard except for the general matters in clause 4, the analytical method in clause 5 and the preparation of sample in clause 6.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

- JIS K 0050 *General rules for chemical analysis*
- JIS K 0113 *General rules for methods of potentiometric, amperometric, coulometric, and Karl Fischer titrations*
- JIS K 0130 *General rules for electrical conductivity measuring method*
- JIS K 0211 *Technical terms for analytical chemistry (General part)*
- JIS K 0212 *Technical terms for analytical chemistry (optical part)*
- JIS K 0213 *Technical terms for analytical chemistry (Electrochemistry part)*
- JIS K 0215 *Technical terms for analytical chemistry (Analytical instrument part)*
- JIS K 0557 *Water used for industrial water and wastewater analysis*
- JIS K 1101 *Oxygen*
- JIS K 8001 *General rule for test methods of reagents*
- JIS R 1306 *Porcelain combustion boats for chemical analysis*
- JIS R 1307 *Porcelain combustion tubes for chemical analysis*
- JIS Z 2615 *General rules for determination of carbon in metallic materials*
- JIS Z 8402-1 *Accuracy (trueness and precision) of measurement methods and results — Part 1 : General principles and definitions*
- JIS Z 8402-2 *Accuracy (trueness and precision) of measurement methods and results — Part 2 : Basic method for the determination of repeatability and reproducibility of a standard measurement method*
- JIS Z 8402-3 *Accuracy (trueness and precision) of measurement methods and re-*

sults — Part 3 : Intermediate measures of the precision of a standard measurement method

JIS Z 8402-4 *Accuracy (trueness and precision) of measurement methods and results — Part 4 : Basic methods for the determination of the trueness of a standard measurement method*

JIS Z 8402-5 *Accuracy (trueness and precision) of measurement methods and results — Part 5 : Alternative methods for the determination of the precision of a standard measurement method*

JIS Z 8402-6 *Accuracy (trueness and precision) of measurement methods and results — Part 6 : Use in practice of accuracy values*

JIS Z 8801-1 *Test sieves — Part 1 : Test sieves of metal wire cloth*

3 Terms and definitions

For the purpose of this Standard, the terms and definitions given in JIS K 0211, JIS K 0212, JIS K 0213 and JIS K 0215 and the following apply.

3.1 lance

a carrier pipe which supplies oxygen efficiently to just above the sample for accelerating the combustion of sample

4 General matters

The general matters shall be as follows.

- a) General matters of chemical analysis shall be in accordance with JIS K 0050.
- b) General matters of electrical conductivity measuring method shall be in accordance with JIS K 0130.
- c) General matters of coulometric titration shall be in accordance with JIS K 0113.
- d) Water supplied for analysis shall be of the type and quality of A3 or A4 as defined in Annex 1 of JIS K 0050 or clause 4 of JIS K 0557.
- e) All the reagents used shall be of the highest class specified in respective relevant JIS standards, if there is any, or be of an appropriate quality. Reagents for which there is no relevant JIS standard shall be of such a quality as not interfering with the analysis. For trace analysis, reagents of especially high purity shall be used.
- f) The apparatus and implement to be used shall satisfy the designated functions.

5 Analytical method

Sample is decomposed by either the wet type decomposition method or the dry type

decomposition method. The analytical methods falling under each type of these decomposition methods shall be as follows.

- a) **Wet type decomposition method** Sample is decomposed with acid or flux, so that sulfur is made into sulfuric acid, then determination according to the following method of measurement is conducted. These analytical methods shall be in accordance with individual standards.
- 1) **Gravimetric method** With an interfering element, if contained, removed or made so as not to inhibit, barium chloride is added to the acidic solution of hydrochloric acid to make precipitate of barium salt, which is then filtered, washed, dried, incinerated, ignited, made to be a constant weight, and its mass is obtained. This method is generally applied to samples of sulfur content not less than 0.005 % (mass fraction).
 - 2) **Reduction distillation methylene blue absorptiometry** A reducing agent is added and distilled to separate as hydrogen sulfide, and *N,N*-dimethyl-*p*-phenylene diammonium and iron (III) are added to produce methylene blue, the absorbance of which is obtained. This method is generally applied to samples of sulfur content 0.001 % (mass fraction) or over to and excluding 0.03 % (mass fraction).
- b) **Dry type decomposition method** Sample is burnt singly or together with a combustion improver in a stream of oxygen to oxidize sulfur to produce sulfur dioxide, which is separated from other coexisting gases and determined. This analytical method is classified into the following according to the measuring system.
- 1) **Sodium hydroxide titration method** Sulfur dioxide, etc. in combustion gas is absorbed in hydrogen peroxide to produce sulfuric acid, which is then titrated with sodium hydroxide solution and the amount of titration is obtained. This method is generally applied to samples of sulfur content not less than 0.005 % (mass fraction).
 - 2) **Potassium iodate titration method** Sulfur dioxide in combustion gas is absorbed in hydrochloric acid and titrated with potassium iodate solution, and the amount of titration is obtained. This method is generally applied to samples of sulfur content not less than 0.005 % (mass fraction).
 - 3) **Electrical conductivity method** Sulfur dioxide in combustion gas is absorbed in hydrogen peroxide to make sulfuric acid and the change of electrical conductivity of this solution is obtained. This method is generally applied to samples of sulfur content not less than 0.001 % (mass fraction).
 - 4) **Coulometric method** Sulfur dioxide in combustion gas is absorbed in weakly acidic solution. This solution is then electrolyzed and the electrical quantity required to return it to the original pH is obtained. This method is generally applied to samples of sulfur content not less than 0.001 % (mass fraction).
 - 5) **Infrared absorption method** Sulfur dioxide in combustion gas is sent to the infrared absorption cell and the infrared absorption amount by sulfur dioxide is continuously measured and integrated (integration method) or the maximum definite

infrared absorption value is obtained (circulation method).

This method is generally applied to samples of sulfur content not less than 0.001 % (mass fraction).

6 Preparation of samples

6.1 Classification of samples

Samples dealt with in this Standard are classified as follows according to the state before preparation.

Sufficient care shall be taken in preparing samples, especially not to allow segregation of sulfur, contamination or degeneration, so that the sample prepared will represent the average composition of the whole lot.

- a) Samples taken from molten metal
- b) Massive, cylindrical, linear, plate and foil type samples
- c) Sponge type samples
- d) Powdery samples

6.2 Machine, tool and implement

The machine, tool and implement used for preparing samples shall be as follows.

- a) **Machine** Lathe, shaping machine, drilling machine, crusher, edge runner mill, stamp mill, compressor, etc.
- b) **Tool** Drill, cutting tool, cutting plier, cutting nippers, cutter, scissors, mortar, hammer, etc.
- c) **Implement** Scoop, spoon, riffle sampler, sieve, stainless steel container, dies, punch, magnet, etc.

The machines, tools and implements shall be cleaned well before use. Especially, the parts which would come into contact with the sample shall be washed to be maintained clean so as not to contaminate samples. For cleaning, ethanol, acetone, diethylether, etc. shall be used while paying attention to exhaust.

6.3 Preparation of analytical samples from different forms of materials

6.3.1 Preparation from sample taken from molten metal

Preparation from sample taken from molten metal by casting or other method shall be as follows.

- a) Sample taken is removed of foreign matter, oxide, etc. adhered on the surface by means of an adequate machine such as drilling machine, and then continuously drilled to make shavings of thickness under 1 mm. These shavings are mixed well and then reduced, if necessary, to serve as an analytical sample. The pressure and rotational speed of drilling shall be such that the surfaces of resultant shavings are

not oxidized. Lubricants such as oils and fats shall not be used. Water pouring for the purpose of cooling the sample shall not be performed. Further, care shall be taken so that the abraded powder of drill, etc. is not mixed in the shavings.

- b) Shavings in the state of cords, if produced, are made into smaller pieces by using an adequate tool such as a mortar or scissors, mixed well, and then reduced, if necessary, to serve as an analytical sample.

6.3.2 Preparation from massive, cylindrical, linear, plate and foil type samples

Preparation from massive, cylindrical, linear, plate and foil type samples shall be in accordance with one of the followings.

a) Where machining or cutting is suitable

- 1) For massive, cylindrical, linear and plate samples, preparation shall be according to 6.3.1 a) or b).
- 2) For thin wire and foil type samples, after a new surface is washed with ethanol or diethylether, samples are cut into smaller pieces by means of scissors or other similar tool, and mixed well and reduced, if necessary, to serve as analytical sample.

b) Where crushing is suitable

- 1) For massive samples, the whole amount thereof is crushed to particles of most appropriate coarseness by using a crusher, stamp mill, mortar, etc., then they are reduced according to the increment reduction method, riffle sampler, etc.

Care shall be taken that loss of fragments or mixing of foreign matters does not occur during the course of crushing or reduction

- 2) Crushing, mixing and reducing are repeated with cares to maintain the average composition of the original sample, and the crushed sample is supplied for analysis.

c) Other cases Preparation of samples that are difficult to machine, cut or crush shall be as follows.

- 1) The mass of sample is smashed and a portion of some of the fractured surfaces is cracked to be collected, which are then repeatedly smashed, mixed and reduced while taking care so as to maintain the average composition of the original sample, to serve as an analytical sample.
- 2) In the case of a sample mass of which the segregation is considered negligible, a portion of it is cracked to be collected, and then crushed to serve as an analytical sample.

6.3.3 Preparation from sponge type samples

Preparation from sponge type samples shall be as follows.

- a) A portion of the sample is taken such that the particle size is as uniform as possible. The taken portion is then put in a die, pressed by a punch inserted from above and

moulded by applying suitable pressure by a compressor.

- b) The compressed mass is taken out and the shavings are made by means of a lathe or a drilling machine, etc. under such a pressure and at a rotational speed that the surfaces of resultant shavings will not be oxidized.

In the case of using a machine with which cutting in a stream of argon is possible so that oxidization can be avoided, the cutting speed should be increased.

- c) Shavings are collected in a stainless steel container, etc., and then smashed with a stainless steel rod or spoon, passed through a sieve whose nominal aperture is principle size 4 mm as specified in **JIS Z 8801-1**, and mixed well to serve as an analytical sample.

6.3.4 Preparation from powdery samples

Preparation from powdery samples shall be as follows.

- a) After mixing well, a portion of it is taken to serve as an analytical sample.
- b) If the powdery sample requires crushing, it is subjected to repeated crushing, mixing and reducing performed with cares to maintain the average composition of the original sample, to serve as an analytical sample.

6.4 Handling of analytical sample

Handling of analytical samples shall be as follows.

- a) When it is possible for the surface of sample to be contaminated with oil, etc, in the course of preparation, it is washed with ethanol, diethylether, etc, before stored.

Further, when it is possible for iron powder, etc. to have been mixed during the course of preparation, if separation with a magnet or similar means is possible, it should be removed using a magnet.

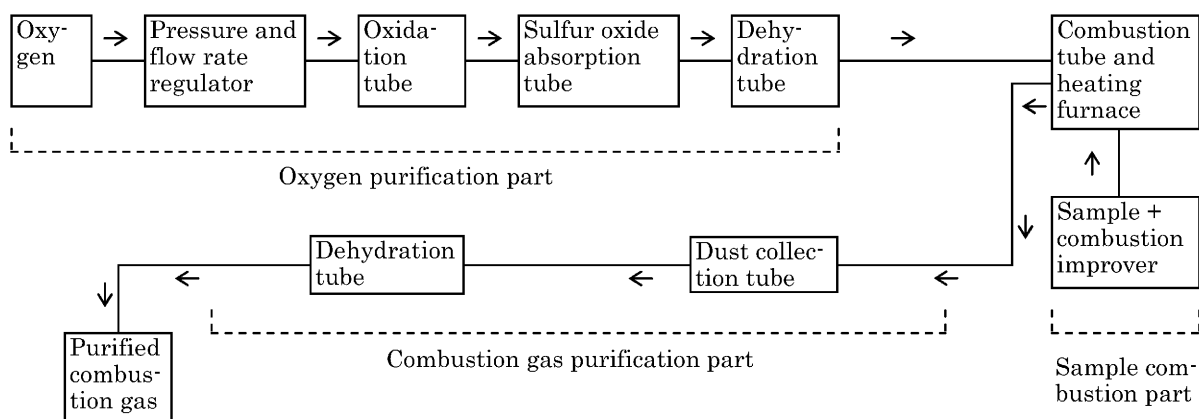
- b) The analytical sample is, as a rule, stored in a hermetically sealed clean glass bottle. When the analytical sample of material which can be easily oxidized is to be preserved for a long period of time, air in the bottle is previously replaced with inert gas such as argon.
- c) When weighing out analytical sample from sample for analysis, the sample is mixed so as to maintain the average composition, and a clean stainless steel spoon or similar tool is used so that sample is not contaminated.

7 Classification of apparatus

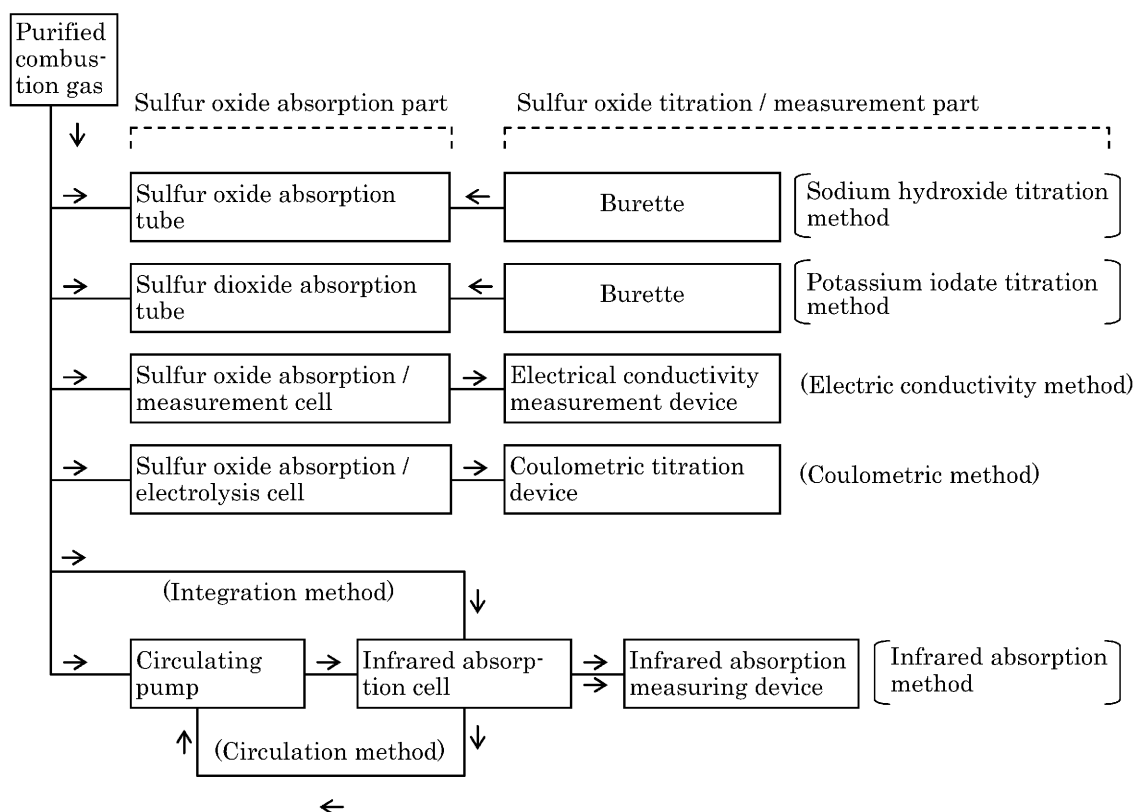
7.1 Composition of apparatus

In the dry type decomposition method, the apparatus, by which sulfur in sample is oxidized to sulfur oxide, is largely divided into the sulfur extraction part and the sulfur oxide determination part. Figure 1 shows an example of composition of an apparatus for sulfur determination method. The sulfur extraction part consists of the oxygen purification part, sample combustion part and combustion gas purification part, and the

sulfur oxide determination part consists of the absorption part of combustion gas and the titration apparatus or measuring instrument thereof. The composition of sulfur oxide determination part varies depending on the measurement system specified in clause 5.



a) Sulfur extraction part



b) Sulfur oxide determination part

Figure 1 Example of composition of apparatus for sulfur determination method

7.1.1 Oxygen purification part

This part controls the pressure and flow rate of oxygen supplied from oxygen cylinder and removes the components to be the inhibitor of sulfur determination such as sulfur oxide, organic sulfur compounds, water, etc. contained in oxygen, and consists of an oxygen cylinder, pressure and flow rate regulator, oxidation tube, sulfur oxide absorption tube or sulfur oxide absorption column, dehydration tube or dehydration column, all connected in this order for use.

Moreover, in the case of a dry oxidation tube, the electric resistance heating furnace which heats the oxidation tube is used.

7.1.2 Sample combustion part

This part heats and burns the sample in a stream of oxygen and consists of a sample inserting part, combustion tube and heating furnace. For the combustion tube, there are those made of porcelain and those made of quartz glass, and for the heating furnace, there are those of the electric resistance heating system and those of the high frequency induction heating system. The inlet of the sample combustion part is connected to the oxygen purification part and the outlet is connected to the combustion gas purification part.

7.1.3 Combustion gas purification part

This part, in the case of determining the sulfur oxides in combustion gas, removes the component to be an inhibitor and consists of the dust collection tube and dehydration tube, etc. However, a part of these may be omitted depending on the measuring system. The inlet of combustion gas purification part is connected to the sample combustion part, and the outlet is connected to the sulfur oxide determination part.

7.1.4 Sulfur oxide determination part

This part determines sulfur oxide in purified combustion gas. The composition of this part is different depending on the measuring system, and is as follows.

- a) **Sodium hydroxide titration method** The part consists of the absorption bottle containing neutralized hydrogen peroxide for absorbing the sulfur oxide in purified combustion gas and the burette for titrating the sulfuric acid generated as a result of absorption of sulfur oxide in the absorption bottle with sodium hydroxide solution.
- b) **Potassium iodate titration method** The part consists of the absorption bottle containing hydrochloric acid, potassium iodide and starch solution for absorbing the sulfur oxide in purified combustion gas and the burette for titrating this, while sulfur dioxide is being absorbed in it, with potassium iodate solution.
- c) **Electrical conductivity method** The part consists of the sample cell for absorption of sulfur oxide in purified combustion gas, attached with an electrode for measuring the change of electrical conductivity before and after absorption, and a reference cell, a thermostatic bath for maintaining both cells at a constant temperature, an electrical conductivity measuring circuit and an indicator or recorder.
- d) **Coulometric method** The part consists of the absorption and electrolytic cell in

which the sulfur oxide in purified combustion gas is absorbed and the electrolysis is carried out for returning the pH which has been reduced due to absorption to the original value, a coulometric measuring apparatus to measure the electrical quantity required for electrolysis and an indicator.

- e) **Infrared absorption method** The part is composed of an infrared absorption detector, an infrared absorption measuring circuit and an indicator for measuring the amount of infrared absorption due to sulfur oxide in purified combustion gas. For the measurement of the amount of infrared absorption, the integration method or circulation method is used. In the case of integration method, the combustion gas is released to the atmosphere through the absorption cell. In the circulation method, the circulating pump which circulates combustion gas is used between the infrared absorption cell and the combustion tube.

7.2 Selection of apparatus

The apparatus shall be in accordance with the determination method selected from those specified in 7.1.4 according to the working conditions such as the kind of analytical work, the sulfur content of sample, etc.

For the selection, the following matters shall be considered :

- a) The type of sample (whether many types of samples are to be handled, or only those of the same metal type) ;
- b) The sulfur content (a minute content or a wide range of measurement) ;
- c) The kind of analytical work (e.g. daily work analysis in a factory where many samples are analyzed, an analysis for research where several kinds of samples in relatively small numbers are treated or an analysis for research object where the apparatus is used for only a limited period of time) ;
- d) Sensitivity, accuracy, etc.

7.3 Setting of apparatus

For setting apparatus, the conditions suitable for respective apparatuses shall be satisfied. Generally, an apparatus should be installed in an environment satisfying the following conditions :

- a) There is no corrosive gas, especially no acidic gas and only a minor amount of dust ;
- b) The humidity is not too high and temperature variation is small ;
- c) Variation in the voltage and frequency of the supply power source is small ;
- d) In the case of a high frequency induction heating furnace, sufficient earthing is possible ;
- e) There is only a minor amount of vibration.

7.4 Preliminary operation of apparatus

Prior to the determination operation, the preliminary operation shall be carried out using the analytical sample or a sample similar to the analytical sample to determine