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JAPANESE INDUSTRIAL STANDARD

Methods for Determination of
Sulfur in Iron and Steel

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Methods for Determination of Sulfur
in Iron and Steel

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1. Scope

This Japanese Industrial Standard specifies the methods for determination of sulfur in iron and steel.

2. General Requirements

The general requirements commonly applied for chemical analysis shall conform to JIS G 1201 and JIS Z 2616.

3. Type of Methods

For determination of sulfur in iron and steel, either of the methods as follows shall be applied.

- (1) Gravimetric Method as Barium Sulfate This method shall be subclassified into two methods according to the isolating technique from iron.
 - (a) Extraction Method with MIBK This method shall be applied to the sample which contains 0.005 % and over of sulfur.
 - (b) Isolation Method with Activated Alumina This method shall be applied to the sample which contains 0.003 % and over of sulfur.
- (2) Combustion Method This method shall be subclassified into six methods according to the system for determination.
 - (a) Neutralization Titration Method This method shall be applied to the sample which contains 0.005 % and over of sulfur.
 - (b) Potassium Iodometric Titration Method This method shall be applied to the sample which contains 0.005 % and over of sulfur.
 - (c) Conductometry This method shall be, as a rule, applied to the sample which contains 0.005 % and over of sulfur.
 - (d) Coulometry This method shall be, as a rule, applied to the sample which contains 0.005 % and over of sulfur.
 - (e) Infrared Absorption Method (Integral Method) This method shall be, as a rule, applied to the sample which contains 0.005 % and over of sulfur.
 - (f) Infrared Absorption Method (Circulation Method) This method shall be, as a rule, applied to the sample which contains 0.005 % and over of sulfur.

Applicable Standards:

JIS G 1201-General Rules for Chemical Analysis of Iron and Steel

JIS Z 2616-General Rules for Determination of Sulfur in Metallic Materials

- (3) Absorptiometric Method with Reducing and Distilling Methylene Blue
This method shall be, as a rule, applied to the sample which contains up to 0.05 % of sulfur.

4. Extraction Method with MIBK, Gravimetric Method as Barium Sulfate

4.1 Purport Dissolve the sample by nitric acid and hydrochloric acid which includes potassium chlorate, make evaporation to dryness for removal of nitric acid, remove iron and the like by MIBK with adjusting the concentration of hydrochloric acid, remove nitric acid after dissolving organic substances to be hydrochloric acid solution, add a definite quantity of sulfate ion to form barium sulfate with barium chloride, and then mature the precipitate of barium sulfate with a precipitation flocculant. This precipitate shall be separated by filtration and ignite to determine the mass deeming as barium sulfate.

4.2 Field of Application This method shall be applied only for the analysis of carbon steel.

4.3 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Hydrochloric acid (2 + 1, 1 + 9, 1 + 100)
- (3) Nitric acid whose specific gravity is 1.42 shall be used.
- (4) Hydrofluoric acid
- (5) Potassium chlorate
- (6) Methyl-isobutyl ketone denoted MIBK as an abbreviation.
- (7) Iron: Iron with high purity and does not include over 0.001 % sulfur. When such iron is not available, iron solution which is removed sulfur by the following procedure may be used.

Weigh iron 0.500 g, transfer to a beaker (300 ml), cover with a watch glass, and add 10 ml of hydrochloric acid to heat and dissolve the iron gently. Add 5 ml of hydrogen peroxide water to this solution to oxidize the iron and the like, and continue to heat until it is dried up taking care of stick and sinter. After cooling, add 10 ml of hydrochloric acid (2 + 1), and heat to dissolve the salts followed by cooling down again to room temperature.

This solution shall be deterged and transferred to a separating funnel (200 ml) with approx. 20 ml of hydrochloric acid (2 + 1), and further, added 30 ml of MIBK, shake vigorously for approx. and let stand undisturbed. After the solution is separated into two layers, discard the water phase in the lower layer. Add 20 ml hydrochloric acid (2 + 1) to the organic phase which is left in the separating funnel, shake vigorously for approx. 1 min, and let stand undisturbed. After the solution, is separated into two layers, take off to discard the water phase in the lower layer. Hence, add 20 ml of water to the organic phase which is left in the separating funnel,

shake vigorously for approx. 1 min, and let stand undisturbed. Take off and transfer the water phase in the lower layer to the original beaker. Furthermore, add 10 ml of water to the separating funnel, shake vigorously for approx. 1 min, and let stand undisturbed. Collect the water phase in the lower layer to the original beaker. Discard the organic phase.

Heat the solution collected into the original beaker, boil for approx. 5 min, vaporize almost amount of MIBK which is dissolved in that solution, add 5 ml of nitric acid [4.3 (3)], and dissolve the soluble salts by heating to evaporate.

- (8) Barium chloride solution: Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1 l. This solution which is stood over a period of one night shall be used, provided that this is filtered with filter paper (Class 5 C) when it is used.
- (9) Barium chloride wash solution: Dissolve 1 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 1 l of hydrochloric acid (2 + 100), let stand over a period of one night, and then filter to use with a filter paper (Class 5 C) when it is used.
- (10) Silver nitrate solution (1 w/v %)
- (11) Precipitation flocculant: Add hot water to 5 ml of saturated solution of SEPARAN (polyacrylamide), and cool it. Then dilute it in 100 ml of water.
- (12) Standard sulfur solution (0.05 mgS/ml): Take with weighing 5.4352 g of potassium sulfate (K_2SO_4) which is previously dried at 110 °C and then preserved in a desiccator, dissolve in water, transfer into a 1000 ml measuring flask, dilute with water up to marked line thereof to make up undiluted solution (1.0 mgS/ml). And this shall be diluted in water to make up the volume to 20 times thereof when it is used.

4.4 Weight of Sample Taken Sample shall be taken with weighing depending upon sulfur content in accordance with Table 1.

Table 1

Sulfur content %	Weight of sample taken g
0.005 and over, up to 0.05	10.0
0.05 and over, up to 0.10	5.0
0.10 and over, up to 0.25	2.0
0.25 and over	1.0

4.5 Procedure

4.5.1 Preparation of Sample Solution Transfer the sample taken to a beaker (500 ml), add 1.0 g of potassium chlorate, and cover a watch glass. For 10 g of sample taken, add 50 ml of nitric acid [4.3 (3)], otherwise add gently 30 ml of nitric acid [4.3 (3)] in 2 or 3 ml. While cooling the beaker with water, for 10 g of sample taken, add 50 ml of hydrochloric acid, otherwise add gently 30 ml of hydrochloric acid taking care of the rise of level of solution in the beaker not to boil over. After almost completion of reaction in the beaker, place the beaker at low temperature zone of a hot platen to decompose the sample completely.

4.5.2 Removal of Nitric Acids Transfer the sample solution prepared by 4.5.1 to the hot platen that is kept at approx. 200 °C, and continue heating to evaporate to approx. 20 ml. And then boil it with 30 ml of hydrochloric acid and several drops of hydrofluoric acid ⁽¹⁾, and evaporate by heating to dryness, taking care of sudden boiling over.

Take down the beaker from the hot platen, cool then add 50 ml of hydrochloric acid to the solution, and reheat at low temperature zone of the hot platen to dissolve the soluble salts. Then transfer this on the hot platen that is kept approx. 200 °C, remove the watch glass, continue heating to evaporate to approx. 20 ml.

Take down the beaker from the hot platen, cool somewhat, add 30 ml of hydrochloric acid, dissolve the salts, add water again to approx. 80 ml, filter it with a filter paper (Class 5 A), and rinse thoroughly the residue and the filter paper with hot hydrochloric acid (1 + 9). Collect the filtrate and washing into a beaker (300 ml), heat to evaporate to approx. 30 ml, and then cool it.

Note (1) The amount of hydrofluoric acid to be added shall be adjusted depending on the content of coexisting silicon, while excess addition thereof shall be avoided. In the case of addition, however, hydrofluoric acid shall be dropped directly into the sample solution, taking care of not to adhere the drops to the wall of a beaker.

4.5.3 Removal of Iron and the Like Transfer sample solution obtained by 4.5.2 to a separating funnel (300 ml) with 70 ml of hydrochloric acid (2 + 1), add 120 ml of MIBK, shake vigorously for approx. 1 min, and let stand undisturbed. After the solution is separated into two layers, take off and transfer the water phase in the lower layer to another separating funnel (300 ml), and preserve it as the main solution.

Add 20 ml of hydrochloric acid (2 + 1) to the organic phase which is left in the separating funnel, shake for approx. 30 sec., let stand undisturbed. After the solution is separated into two layers, incorporate the water phase in the lower layer to the main solution which has been preserved previously in another separating funnel. The organic phase which is left shall be treated again with 20 ml of hydrochloric acid (2 + 1), and the water phase obtained shall be incorporated to the main solution. Discard the organic phase.

Add 80 ml of MIBK to the separating funnel which contains the main solution, shake vigorously for 1 min, and extract iron and the like which are left on the funnel. After let the solution stand undisturbed, transfer the water phase in the lower layer to a beaker (500 ml), and preserve it again as the main solution. Add 20 ml of hydrochloric acid (2 + 1) to the organic phase which is left, shake for approx. 30 sec., let stand undisturbed. After the solution is separated into two layers, incorporate again the water phase in the lower layer to the main solution preserved, treat again the organic phase which is left, with 20 ml of hydrochloric acid (2 + 1) in the same manner as mentioned above, and incorporated the water phase to the main solution. Discard the organic phase.

4.5.4 Formation of Precipitate Heat the sample solution obtained by 4.5.3, continue to boil for 10 min, add 10 ml of nitric acid [4.3 (3)], heat successively to decompose organic substances, add 30 ml of hydrochloric acid, and continue to heat and evaporate until just before this solution reaches to dryness. Furthermore, add 15 ml of hydrochloric acid, heat to evaporate, concentrate to remove nitric acid until just before this solution reaches to dryness. Add 20 ml of water to this concentrated solution to dissolve the salts, filter with filter paper (Class 5 C, 9 cm), and deterge with approx. 50 ml of hot hydrochloric acid (1 + 200). Collect the filtrate and washing in a beaker (300 ml). Discard the filter paper and the residue.

Add correctly 10 ml of standard sulfur solution to this solution, heat until just before boiling, immediately agitate with a stirrer and the like under a constant speed so that the solution does not scatter, as well as drop 10 ml of barium chloride solution [4.3 (8)] spending 1 min through a burette, agitate for more 10 min, and let stand for 2 h. Afterwards, add 2 ml of precipitation flocculant [4.3 (11)] being agitated once again, stir it for more 5 min, and let stand overnight.

4.5.5 Weighing of Precipitate The precipitate of barium sulfate obtained by 4.5.4 shall be filtered by filter paper (Class 5 C, 11 cm) with small amount of filter paper pulp. Deterge once the inner wall surface of the beaker with barium chloride wash solution [4.3 (9)], pour wash liquid onto the filter paper, rub off slightly the precipitation adhered on the inner wall surface of the beaker with policeman, wash and transfer onto the filter paper with barium chloride wash solution [4.3 (9)] and deterge 2 or 3 times. Eventually, deterge with hot water until no chlorine ion in the wash liquid is founded by silver nitrate solution (1 w/v %).

Transfer the precipitate and the filter paper into a platinum crucible (No. 30) with known mass, dry and carbonize at lower temperature, incinerate at approx. 500 °C, heat up to 800 °C, and continue to heat for 20 min. Then left the platinum crucible in a desiccator which is having dryer for 20 min and over, cool to room temperature, and measure the mass. In this case, repeat heating and cooling until it becomes to a constant mass.

4.5.6 Blank Test Weigh 0.500 g of iron [4.3 (7)] ⁽²⁾, transfer to a beaker (500 ml), cover with a watch glass, add the same amount of hydrochloric acid as that for the sample little by little, heat to decompose completely, and boil for approx. 10 min. Add the same amount of nitric acid [4.3 (3)] as that for the sample in small quantities to the said solution, boil to remove nitrogen oxide. Hereinafter, apply the same treatments as for the sample according to on and after 4.5.2 ⁽³⁾ to determine blank test values.

Notes (2) Since iron [4.3 (7)] is added to allow the extraction and separation operation easily by MIBK, the amount of sample may be 0.500 g depending on the weight of sample taken. In the case iron solution [4.3 (7)] is used only the procedure on and after 4.5.2 (3) may be applied.

(3) However, does not add hydrofluoric acid.

4.6 Calculation Sulfur content (%) in a sample shall be computed by the following formula:

$$\text{Sulfur } (\%) = \frac{(w-w') \times 0.1374}{W} \times 100$$

where w : mass of barium sulfate obtained by 4.5.5 (g)
 w' : blank test value obtained by 4.5.6 (g)
 W : weight of sample taken (g)

4.7 Accuracy of Determination The accuracy of determination by this procedure shall be as shown in Table 2.

Table 2

Sulfur content %	Standard deviation within laboratory	Standard deviation between laboratory
0.005 and over, up to 0.03	$0.0192 \times [S(\%)] + 0.0002$	$0.0449 \times [S(\%)] + 0.0001$
0.03 and over, up to 0.25 (4)	$0.0186 \times [S(\%)] + 0.0003$	$0.0195 \times [S(\%)] + 0.0007$

Note (4) This figure shows the maximum value of sulfur content of sample used for determination of the accuracy of analysis.

5. Isolation Method with Activated Alumina, Gravimetric Method as Barium Sulfate

5.1 Purport Dissolve the sample with dilute nitric acid or a mixture of dilute nitric acid and hydrochloric acid in the presence of bromine, treat by white fume of perchloric acid after complete decomposition with hydrofluoric acid, and gasification to disperse chromates as the form of chromyl chloride, if necessary. After sulfate ion is absorbed by activated alumina column, elute it with aqueous ammonia, and precipitate barium sulfate with barium chloride from chloric acids solution. Filter to separate this precipitation, ignite and measure the mass as barium sulfate.

5.2 Field of Application This method shall not be applied to such sample that contains selenium.

5.3 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1 + 9, 1 + 19)
- (3) Nitric acid (1 + 1)
- (4) Perchloric acid: When this reagent contains excess part of sulfuric acid, it is necessary to remove this sulfuric acid part through activated alumina column [5.4 (3)].
- (5) Washing of perchloric acid: Dilute 20 ml of perchloric acid [5.3 (4)] in water to 1000 ml.
- (6) Hydrofluoric acid
- (7) Sulfuric acid solution: Add 2.8 ml of sulfuric acid in approx. 500 ml of water carefully, and dilute to 1000 ml with water. Furthermore, dilute 30 ml of this solution to 1000 ml with water. This sulfuric acid solution contains 0.48 mg of sulfur per 10 ml thereof.
- (8) Aqueous ammonia (1 + 19, 1 + 99)
- (9) Bromine
- (10) Ferrous perchlorate solution: Weigh 5.00 g of iron which contains extremely low sulfur, transfer to an Erlenmeyer flask (500 ml), add 25 ml of perchloric acid [5.3 (4)] and 375 ml of water, heat to dissolve within a water bath at 50 °C. When approx. two-thirds of iron is dissolved, take down the Erlenmeyer flask from the water bath, cool and preserve plugging the neck of flask with a rubber stopper being attached a safety valve.
- (11) Barium chloride solution: Dissolve 1.22 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1000 ml. Filter to use with a filter paper (Class 5 C) when it is used. This solution contains 0.16 mg of sulfur per 1 ml thereof.
- (12) Methyl orange solution (0.05 w/v %)

5.4 Apparatus The apparatus shall be as follows:

- (1) Erlenmeyer flask (1,000 ml) for decomposition with a neck for fitting
- (2) Allihn condenser tube (4 to 6 balls type)
- (3) Activated aluminum column (Fig. 1): Fix a column tube to suction-filtering flask, and fill firmly quartz wool with a thickness approx. 20 mm in the lower part of the column tube. Transfer alumina slurry to the column tube to fall the length of alumina column between 100 and 120 mm, wash to drop alumina slurry into the column tube with hydrochloric acid (1 + 19), and press down with quartz wool. In this respect, quartz wool shall contact always with alumina column, and also any part of alumina slurry shall not expose above the quartz wool.