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Determination of Trace Amounts of Sulfur in High-Purity Iron by Infrared Absorption after Combustion: Removal of Sulfur Blank

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In order to determine trace amounts of sulfur in a high-purity iron with the infrared absorption method after combustion, it is necessary to decrease and stabilize sulfur blank on an analytical procedure. Sulfur blank means sulfur species as contaminants which are contained in a reagent, in a ceramic ware and absorbed on surface of an analytical sample and so on employed during an analytical procedure. As a signal of sulfur blank overlaps on a signal of sulfur in an analytical sample and causes error of determination of sulfur in the sample, it needs to be removed before analysis. Sulfur blank is decreased and stabilized by following operations: (a) an accelerator for combustion was heated for 28 min at 1003 K in ambient atmosphere; (b) a ceramic crucible was heated during more than 20 min at 1623 K in ambient atmosphere; (c) oxygen was purified through a gas purifier; (d) an analytical sample was cleaned in an acidic solution. The operation (a) was examined in detail. When a mixture of 0.5 g tungsten with 1.5 g tin as accelerator was heated for over 28 min at 1003 K in ambient atmosphere, sulfur blank value was decreased from 2.75 µg down to 0.94 µg. Consequently, the heating time was fixed for 28 min. As sulfur blank was increased with increasing of mass of an accelerator, its mass was fixed on 2 g. When relationship between sample weight (X axis) and amount of sulfur (Y axis) determined was plotted, the relation became linear. Sulfur content in a sample could be found from a slope of the straight line. By this method, sulfur contents in 3 samples were determined to be 0.71, 1.91 and 1.05 µg/g, respectively. Moreover, sulfur blank on an analytical procedure could be given by the intercept on the Y axis of the straight line. Sulfur blank values were in the range of 1.03–1.11 µg. Sulfur blank values on this manner were very stable for each sample throughout the analytical procedure. When it was defined that detection limit of sulfur was 3 times of standard deviation of sulfur blank and 1 g of a sample was used for analysis, it corresponded to 0.15 µg/g of sulfur.

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1. Introduction

It is well known that trace impurity elements in a high purity iron affects properties of an iron such as ductility, segregation behavior of impurities, corrosion resistance and so on.[1] Trace sulfur is one of impurity elements which mainly affect these properties, therefore, it is necessary to precisely determine trace sulfur in an iron.

A micro amount of sulfur in iron and steel has been determined by infrared absorption method after combustion[2–4] or spectrophotometry.[3,5] In such cases micro amounts of sulfur must be completely separated from iron as main component by following methods, because macro amounts of iron interfere in determination of sulfur.

(a) Dry method: sulfur is separated as sulfur dioxide (SO_2) from a sample by combustion in oxygen flow atmosphere.

(b) Wet method: sulfur is separated as hydrogen sulfide (H_2S) by reduction of sulfate ion (SO_4^{2-}) in acidic solution of sample, after sulfur is transformed into sulfate ion by dissolving of an analytical sample with oxidizing acid. The former is a general method, because reagent solutions are not used and a micro amount of sulfur is rapidly determined in comparison with the latter. In this study, infrared absorption method after combustion in an induction furnace was employed to determine a trace amount of sulfur.

When sulfur blank is high on the analytical procedure, a analytical signal of sulfur of one mass ppm level is not able to be distinguished from sulfur blank. Consequently, the sulfur blank must be decreased to precisely determine a trace amount of sulfur in a high-purity iron.

In the present research, in order to determine sulfur of one mass ppm level, we tried to decrease sulfur blank on an analytical procedure of infrared absorption method after combustion of an analytical sample. Source of sulfur blank seems mainly to be in a ceramic crucible, an accelerator for combustion, oxygen as an atmosphere and contamination of sulfur on a sample surface.

The main experiments were as follows:

(1) Establishment of technique for decreasing a sulfur blank in an accelerator.

(2) Evaluation of a sulfur blank on analytical procedure.

(3) Determination of trace amounts of sulfur in high purity irons.

Sulfur was determined by using both calibration curve and a slope of a straight line which was constructed from relationship between sample weight and sulfur amount. Sulfur blank on an analytical procedure was determined from intercept of the straight line on Y axis.

2. Experimental

2.1 Instrument

In order to determine trace amounts of sulfur in high-purity iron, an analyzer LECO CS-444LS was employed. When an analytical sample was subjected to combustion together with an accelerator in an induction furnace (high frequency:

18 MHz, 2.2 kW) in pure oxygen, sulfur in the sample was transformed to SO_2 and separated from the sample. The SO_2 was determined by absorption of infrared.

A ceramic crucible with a lid was heated in the tube furnace LECO TF-1 in ambient atmosphere at 1623 K to remove sulfur blank in it. An accelerator was heated in a muffle furnace Yamato FP-41 in ambient atmosphere at 1003 K to decrease sulfur blank in it. Oxygen for combustion of a sample was purified through two gas purifiers, which were a purifier LECO CF-10 and a purifier equipped in an analyzer.

2.2 Sample for calibration curve, accelerator and analytical sample

A calibration curve for determination of sulfur was constructed with a certified steel sample LECO JAC 001-051 (sulfur content: 76 ± 5 μg/g, LECO Corp.).

An accelerator for combustion was consisted of mixture of granulated tungsten Lecocel II HP (LECO Corp.) 0.5 g and granulated tin (LECO Corp.) 1.5 g.

Sulfur in three iron samples was determined: a high-purity electrolytic iron A-Iron (plate, home-made, $RRR_H = 1570$), a low sulfur iron powder LECO 501-078 (granular, LECO Corp.) and high purity iron JSS 001-4 (chip, sulfur content: 1.9 μg/g, The Japan Iron and Steel Federation).

2.3 Cleaning of sample

When an iron sample was a solid mass, pieces of the sample for analysis were cut off from the solid mass sample and cleaned according to the report[6] at the meeting of UHPM-97; pieces of an iron sample were chemically etched for one min in a mixture of hydrofluoric acid (7.5 mL), hydrogen peroxide (125 mL) and distilled water (15 mL) cooled at 273 K. Then the sample was transported to a mixture of hydrogen peroxide (50 mL) and distilled water (50 mL) to stop etching. The sample was sufficiently washed in distilled water with an ultrasonic cleaner and subsequently in ethanol in a similar manner, and then dried in ambient atmosphere. This cleaning procedure was proposed by Abiko *et al.*[7]

2.4 Analytical procedure of sulfur

Schematic analytical procedure of trace amounts of sulfur in high purity irons is shown in Fig. 1. A ceramic crucible with a lid was previously heated in a tube furnace for 20 min in ambient atmosphere at 1623 K to remove sulfur blank in it. After cooling of the crucible, a mixture of tungsten 0.5 g and tin 1.5 g as an accelerator for combustion was placed in the crucible. After they were heated in a muffle furnace for about 7 min in ambient atmosphere at 1003 K, and taken out from the furnace. Immediately, the accelerator in the crucible was stirred with a platinum rod for about 1 min, and then again heated for 21 min in the muffle furnace. Therefore, the summation of heating time was about 28 min. They were taken out from the furnace. After standing them for about 3 min, an analytical sample was placed on a hot accelerator, and then they were stood for 1 min. They were set at an induction furnace in an analyzer to determine sulfur in a high purity iron.

Evaluation of sulfur blank on the analytical procedure was performed without an iron sample by a similar manner to analysis of the sample, and by reading off the value of intercept of a straight line at Y axis which was drawn from relationship between sample weight and sulfur amount.

Calibration curve was constructed from two determined points without and with Calibration Standard Steel Sample, LECO JAC 001-051, according to the analytical procedure as

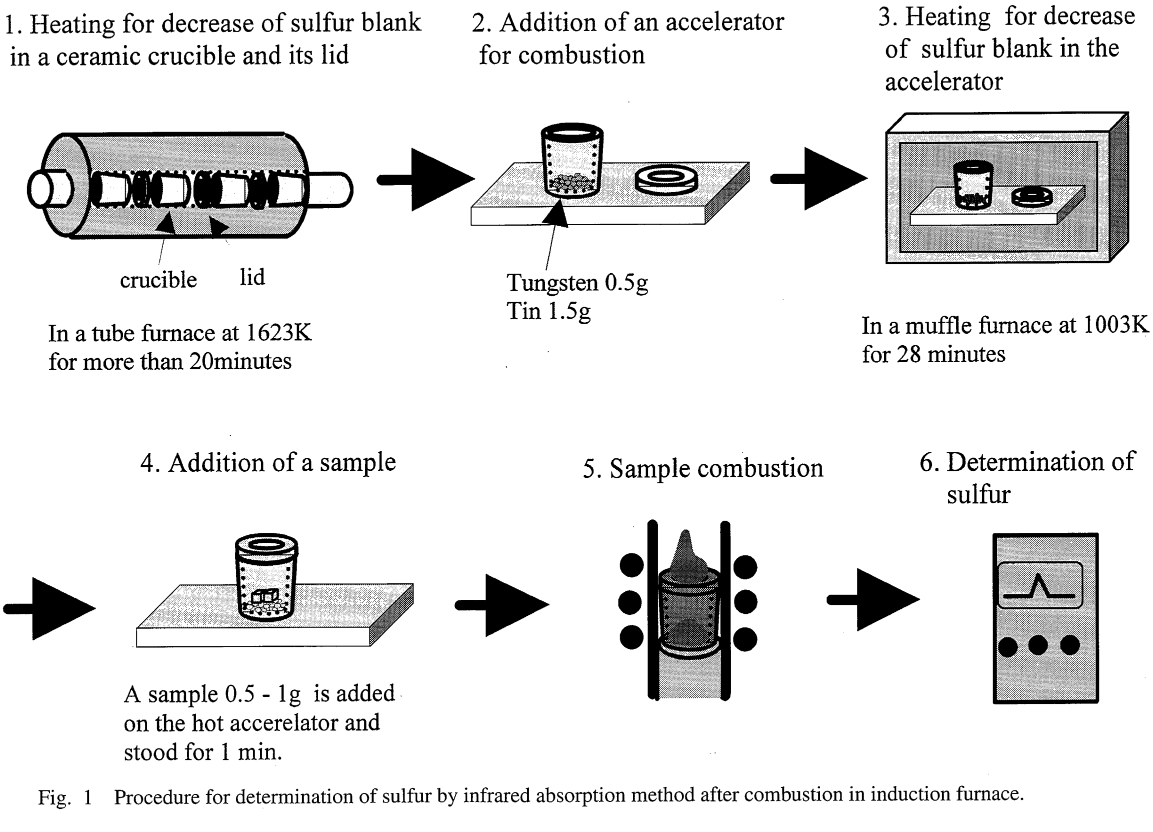

Fig. 1 Procedure for determination of sulfur by infrared absorption method after combustion in induction furnace.

described above except the procedure of cleaning of a standard sample.

3. Results and Discussion

3.1 Removal of sulfur blank in accelerator

Sulfur blank interfered in determination of trace sulfur in a sample, because an analytical signal of trace sulfur in it overlapped on a sulfur blank signal and was not separated from its blank signal.

Sulfur blank mainly consisted of sulfur in a ceramic crucible, an accelerator and oxygen. When a ceramic crucible was heated at 1623 K in ambient atmosphere and oxygen was passed through two purifiers, sulfur blank in them was removed. In order to remove sulfur blank in an accelerator, an accelerator was heated at 1003 K. An accelerator consisted of a mixture of tungsten 0.5 g and tin 1.5 g. However, in spite of increase of heating time for an accelerator, sulfur blank in an accelerator was not able to be removed by heating. The effect of heating time on sulfur blank is shown in Fig. 2. An accelerator was heated for 7 min, taken out from the muffle furnace, stirred with a platinum rod and then again heated for 7, 14, 21, 28 or 35 min, respectively.

As shown in Fig. 2, sulfur blank was determined to be 2.75 μg without heating. Sulfur blank decreased with increasing in heating time and became the same value of 0.94 μg after heating for 28, 35 and 42 min. The sulfur blank 0.94 μg was average value of 9 times of analysis. The standard deviation in determination was ±0.068 μg and its relative standard deviation (repeatability) was 7.2%.

It is concluded from this experimental result that the most suitable heating condition of an accelerator 2 g was for 28 min at 1003 K in ambient atmosphere. Here, it must be noted that an accelerator was not available for combustion of an analytical sample when its heating time was more than 60 min, because a large portion of an accelerator was transformed to oxide by heating in oxygen and induction current was not able to be generated to oxide.

3.2 Amount of accelerator on sulfur blank

Sulfur blank in an accelerator was not able to be completely removed by heating it as described above. Consequently, it was presumed that sulfur blank was increased with increasing of the amount of an accelerator. This is shown in Fig. 3. Ratio of weight of tungsten to tin as an accelerator was constant 1 to 3. Therefore, it was necessary for stable sulfur blank to weigh precisely an accelerator and to heat an accelerator for precise time and at precise temperature.

3.3 Determination of sulfur in high-purity irons

According to the analytical procedure [2.4], trace amounts of sulfur in three kinds of iron described in [2.2] were determined. The mass of an analytical sample was from 0.25 to 1.50 g. Analysis of each sample was repeated 10, 15 and 12 times for A-Iron, JSS 001-4 and LECO 501-078, respectively. Sulfur contents in these samples were found to be 0.71 ± 0.038, 1.91 ± 0.054 and 1.02 ± 0.057 μg/g, and the relative standard deviations were 5.4, 2.8 and 5.6%, respectively.

When it was defined that a detection limit of sulfur was 3 times of a standard deviation of an analytical value, it was 0.2 μg/g.

On the other hand, attempt was made to determine sulfur content by other evaluation method. When relationship between weight of an analytical sample (X axis) and amount of sulfur determined was linear, a slope of the straight line indicated sulfur content in the sample, and an intercept at Y axis of the straight line suggested sulfur blank on an analytical procedure. The method was explained from a straight line as shown in Fig. 4.

The method was applied to determination of trace sulfur in three samples, *e.g.*, A-Iron, JSS 001-4 and LECO 501-078.

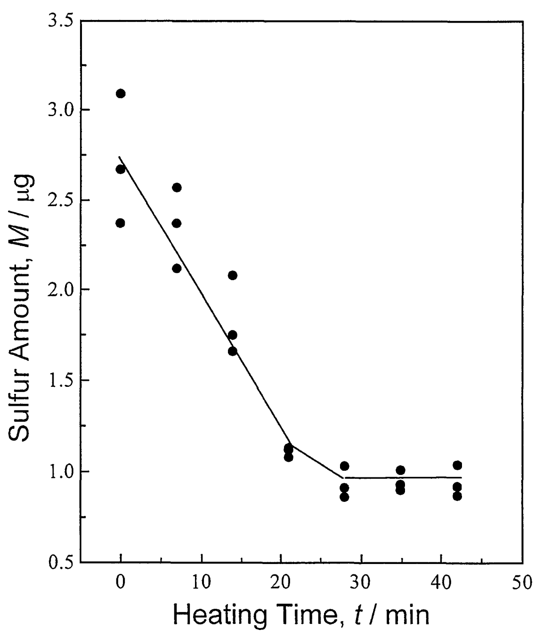

Fig. 2 Effects of heating time on sulfur blank in accelerator. Accelerator: tungsten 0.5 g and tin 1.5 g. Heating temperature: 1003 K.

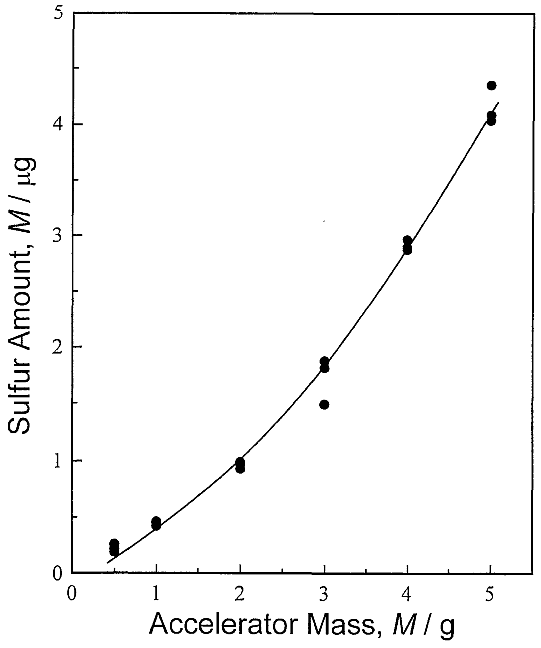

Fig. 3 Relationship between accelerator weight and sulfur blank after heating for 28 min at 1003 K. Ratio of tungsten to tin = 1 to 3.

The relationships between sample mass (X axis) and sulfur amount (Y axis) are shown in Fig. 5. The equation of the straight line for each sample is shown in Table 1. The equation was calculated by the least squares method. It was found from the slopes of the equations that sulfur contents in A-Iron, JSS 001-4 and LECO 501-078 were 0.71, 1.91 and 1.05 µg/g, respectively.

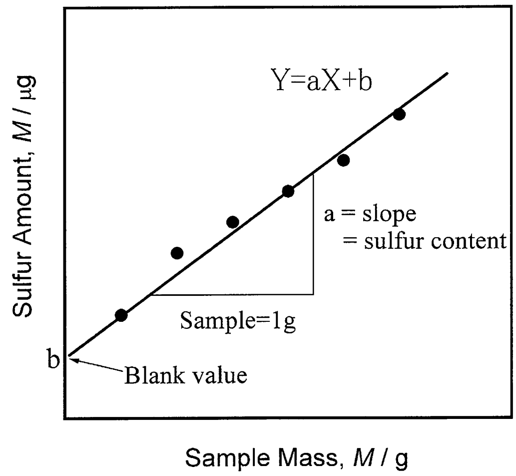

Fig. 4 Sulfur content and sulfur blank derived from relationship between sample weight and sulfur amount in high purity iron.

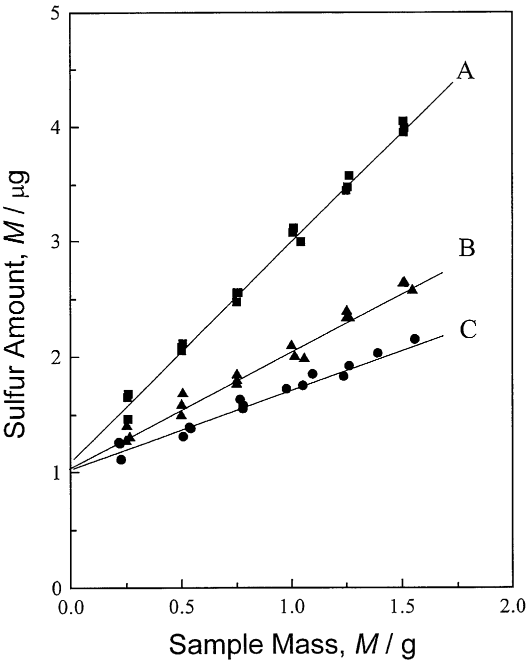

Fig. 5 Relationship between sample weight and sulfur amount in high purity iron. Sample: A; JSS 001-4, B; LECO 501-078, C; A-Iron.

3.4 Evaluation of sulfur blank on analytical procedure

Moreover, the intercepts of a straight line at Y axis in Fig. 5 gave the values of sulfur blank, namely 1.03, 1.11 and 1.03 µg for each sample, respectively. These values were shown on second term of the right side of the equation in Table 1. The average value of these intercepts was 1.06 µg. As described in 「3.1」, the sulfur blank in an accelerator, a crucible with a lid and flowing oxygen was 0.94 µg. The difference of sulfur blank from these experimental procedure, 0.12 µg, seems to be negligible, because it was difference in the range of detection limit of an analytical method used. In short, sulfur blank on an analytical procedure was very stable. Detection limit of sulfur was 0.15 µg/g, when it was defined as 3 times of standard deviation of sulfur blank shown in Table 1.

4. Conclusion

In order to analyze a trace amount of sulfur in high-purity iron by infrared absorption method after combustion in induction furnace, it was important that sulfur blank on analytical procedure was decreased or removed. Mainly, by heating of an accelerator for combustion in ambient atmosphere, sulfur blank in it was decreased and its value became stable. In the present research, the analytical method of a trace amount of sulfur less than or equal to 1 µg/g in high-purity iron was established.

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Table 1 Analytical results of sulfur in high-purity iron.

Sample		Equation of straight line in Fig. 5	*r* (coefficient of correlation)	S found µg/g	S blank µg	S certified µg/g
Pure iron: JSS 001-4 (chip)	A	$Y = 1.91X + 1.11$	0.9867	1.91	1.11	1.9
Low sulfur iron: LECO 501-078 (powder)	B	$Y = 1.05X + 1.03$	0.9973	1.05	1.03	—
High purity electrolytic iron: A-Iron (plate)	C	$Y = 0.71X + 1.03$	0.9872	0.71	1.03	—