

# Determination of Trace Element Quantities in Ultra High-Purity Iron by Spectrochemical Analysis after Chemical Separation \*

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When trace elements in an ultra high-purity iron were determined, an analytical blank on a chemical analysis interfered with the determination of them. Similarly, the existence of major component in a sample interfered with the determination of trace elements. Therefore, in order to determine trace elements, it was examined that how to remove or decrease an analytical blank and how to separate trace elements from major component of a sample. For example, when C and S in an ultra high-purity iron were determined by combustion/infrared absorption method, an accelerator for combustion of an analytical sample contained C and S as blank. The accelerator consisted of a mixture of tungsten and tin. By heating it in ambient atmosphere, carbon blank was removed to be zero and sulfur blank was decreased to lower level. Consequently, when detection limit was defined as a value corresponding to 3 times of the standard deviation of blank value, it of carbon was infinitesimal and it of sulfur was  $0.2 \mu\text{g g}^{-1}$ . Infinitesimal detection limit of carbon resulted from zero of the blank value of carbon. For that reason, detection limit of carbon was read as  $0.01 \mu\text{g g}^{-1}$  of carbon that was minimum scale for carbon on the analytical instrument, because the standard deviation of the blank value could not to be calculated. Independently, in order to determine trace Sn, Ag and Au in a high-purity iron, these elements were separated from major component (iron) by co-precipitation. Metallic Pd was used as co-precipitant. Metallic Pd had been rarely used as co-precipitant. The elements were determined by electrothermal atomic absorption spectrometry (ET-AAS). When these elements were detected by ET-AAS, the Pd was available as chemical modifier. By the separation, content  $0.002\text{--}0.02 \mu\text{g g}^{-1}$  of the elements was determined.

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## 1. Introduction

Recently, in order to develop metallic materials with new properties, ultra high-purity metals have been used as raw materials. Consequently, purification of various metals has been investigated. Abiko and Takaki have made an ultra high-purity iron by purification of an electrolytic iron. They showed<sup>1-8)</sup> that properties of the ultra high-purity iron were different from those of a non-purified iron. Moreover it became clear that differences of the properties were correlated with different of purify between these irons. Therefore it is necessary that purity of an ultra high-purity iron is evaluated.

An ultra high-purity iron contains trace amounts of elements as impurities. However, by purification, each element as impurities in the iron was lowered below about  $1 \mu\text{g g}^{-1}$  so-called 1 mass ppm. Each element as impurity in an ultra high-purity iron was usually determined by chemical analysis<sup>9-14)</sup> and then purity of it is evaluated<sup>2,8,9,14,15)</sup> by subtraction of summation of analytical values of each element from 100 mass%. Analytical methods of each element were shown as certified methods in JIS<sup>16,17)</sup> (Japanese Industrial Standard), ISO<sup>18)</sup> (International Organization for Standardization) and ASTM<sup>19,20)</sup> (American Standard for Testing and Materials) and others. However, contents of trace elements in an ultra high-purity iron are so low that these methods do not apply to the iron as they are. Analytical methods are necessary to determine each trace element in it. Therefore, it is purpose of experiment that analytical methods for determina-

tion of trace elements in it.

Requirements for analyses of trace elements are: (1) high sensitivity (selection of highly sensitive analyzer), (2) reliability (selection of an analytical method based on mass), (3) decrease in noise and background signals (optimum conditions for operation of analytical instrument), (4) decrease in blank value during analysis (improvement of analytical procedure), (5) removal of interfering factors (chemical separation of trace elements from major component). In this paper, (4) and (5) described above are reported. As example about (4), it was shown that decrease of analytical blank was effective for determination of trace amounts of C and S by combustion/infrared absorption method. As example about (5), it was shown that separation of trace amounts of Sn, Au and Ag from iron as major component brought to low detection limit of them for determination of them by electrothermal atomic absorption spectrometry.

## 2. Experimental

### 2.1 Instrument

An analyzer, LECO CS-444LS, was used for determination of trace amounts of C and S in an ultra high-purity iron by combustion/infrared absorption method. A tube furnace, LECO TF-1, was utilized to decrease blank value in ceramic crucibles. A muffle furnace, Yamato FP-41, was used to decrease carbon and sulfur blanks in an accelerator for combustion of an analytical sample. A gas purifier, LECO CF-10, was employed to remove CO, CO<sub>2</sub> and hydrocarbon in oxygen helping combustion. Polarized simultaneous multi-element atomic absorption spectrophotometer,

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Hitachi Z-9000, was used to detect atomic absorption signals with a graphite-tube.

## 2.2 Reagent and sample

An accelerator for combustion of an analytical sample was a mixture of tungsten (granular. LECOCEL II HP, LECO Corp.) and tin (granular. LECO Corp.).

Calibration curves for determination of C and S were constructed with a certified steel sample LECO JAC 001-051 (C:  $78 \pm 5 \mu\text{g g}^{-1}$ , S:  $76 \pm 5 \mu\text{g g}^{-1}$ , LECO Corp.). Analytical samples were JSS 001-4 (Pure iron, C:  $2.5 \mu\text{g g}^{-1}$ , S:  $1.9 \mu\text{g g}^{-1}$ . Japanese Iron and Steel Certified Reference Materials), JSS 1201-1 (Steel for determination of C, C:  $5 \mu\text{g g}^{-1}$ ), A-Iron (High-purity electrolytic iron,  $\text{RRR}_H = 1570$ . Toho Zinc Co. Ltd.) and LECO 501-078 (Low sulfur iron powder. LECO Corp.).

## 2.3 Analytical procedure

### 2.3.1 Determination of C and S by combustion/infrared absorption method

Analytical procedures<sup>21,22)</sup> were previously described in detail. They are briefly given here. A ceramic crucible was preliminarily degassed by heat at 1623 K for 20 min in ambient atmosphere. An accelerator for combustion was placed in the ceramic crucible. The accelerator consisted of a mixture of tungsten (1.5 g) and tin (0.5 g) for determination of C, and a mixture of tungsten (0.5 g) and tin (1.5 g) for S. The mixture for determination of C was heated for 5 min at 1003 K in a muffle furnace, taken out from the furnace, stirred with a platinum wire for 10 s and heated again for 5 min in the furnace. The heat and stir were alternately repeated three times, respectively. Therefore, summation of heating time was 15 min. The mixture for determination of S was heated continuously for 28 min at 1003 K in a muffle furnace. After heat of the mixture, 0.25–1.5 g of an analytical sample was put on it. The sample was set in the analyzer for determination of C and S together with accelerator in the crucible. Radio frequency power was supplied for combustion of the sample. If necessary, an iron sample was cut into pieces of the sample, and they were cleaned accordingly to the reports.<sup>23,24)</sup>

### 2.3.2 Analytical procedure of Sn with and without chemical separation

In case of no separation of Sn: One gram of an iron sample was dissolved in a mixture of 20 ml of 7 mol/l nitric acid and 20 ml of 6 mol/l hydrochloric acid. After 5 ml of phosphoric acid (7 mol/l) was added to the sample solution, the solution was exactly filled up to 100 ml with distilled water. Ten  $\mu\text{l}$  of the solution was injected into a graphite-tube furnace attached to atomic absorption spectrophotometer. Tin was heated and atomized in order of dry (at 353–423 K for 30 s), ash (at 423–1573 K for 30 s, next at 1573 K for 30 s) and atomization (at 3073 K for 5 s), and then atomic absorption of Sn was determined at 224.6 nm.

Calibration curve was constructed using solution prepared by mixing of solution of iron (containing 1 g as iron) and solution of Sn (addition of 0–50  $\mu\text{g}$  Sn). Nitric, hydrochloric and phosphoric acids were contained in this solution. The iron used was produced by Toho Zinc Co. Ltd. and contained  $1.0 \pm 0.1 \mu\text{g g}^{-1}$  of Sn which was determined by electrothermal atomic absorption spectrometry.

In case of separation<sup>25)</sup> of Sn from pure iron: One gram of an iron sample was dissolved in a mixture of hydrochloric and nitric acids. A mixture of sulfuric acid and phosphoric acid was added to the solution and the solution was heated to generate fume of sulfuric acid. After iron was masked with EDTA-Na solution at pH 4.0 by boiling, it was reduced with 1 g of ascorbic acid. Palladium solution (3 mg as Pd) was added to the solution. The solution was adjusted to pH 10.0 with NaOH solution, and then Sn and Pd were reduced with sodium tetrahydroboric acid ( $\text{NaBH}_4$ ) solution to be converted to their metals. After the metals were in a mixture of 1 ml of nitric acid, 0.2 ml of hydrochloric acid and 1 ml of tartaric acid (10% m/m), the solution was exactly filled up to 10 ml with distilled water. Ten  $\mu\text{l}$  of the solution was injected into a graphite-tube furnace attached to atomic absorption spectrophotometer. Tin was heated and atomized in order of dry (at 353–423 K for 30 s), ash (at 423–1873 K for 30 s, next at 1873 K for 30 s) and atomization (at 2973 K for 5 s), and then atomic absorption of Sn was determined at 224.6 nm. Nitric acid and hydrochloric were contained in this solution.

Calibration curve was constructed using solution prepared by mixing of solution of Pd (3 mg of Pd), solution of Sn and 1 ml of tartaric acid (10% m/m). Nitric acid and hydrochloric acid were contained in this solution.

### 2.3.3 Analytical procedure of Au and Ag with and without chemical separation

In case of no separation of Au and Ag: One gram of an iron sample was dissolved in a mixture of nitric acid and hydrochloric acid. The solution was exactly filled up to 100 ml with distilled water. Ten  $\mu\text{l}$  of the solution was injected into a graphite-tube furnace attached to atomic absorption spectrophotometer. Au was heated and atomized in order of drying (at 353–423 K for 30 s), ashing (at 423–1273 K for 30 s, next at 1273 K for 30 s) and atomizing (at 2773 K for 5 s), and then atomic absorption of Au was determined at 242.8 nm. Ag was heated and atomized in order of dry (at 353–423 K for 30 s), ash (at 423–1073 K for 30 s, next at 1073 K for 30 s) and atomization (at 2673 K for 5 s), and then atomic absorption of Ag was determined at 328.1 nm.

Calibration curve was constructed using solution prepared by mixing of solution of iron (containing 1 g as iron) and solutions of Au and Ag. Nitric acid and hydrochloric acid were contained in this solution. The iron used was produced by Toho Zinc Co. Ltd. and contained below  $0.003 \mu\text{g g}^{-1}$  of Au and below  $0.002 \mu\text{g g}^{-1}$  of Ag which were determined by electrothermal atomic absorption spectrometry after separation with co-precipitation.

In case of separation<sup>26)</sup> of Au and Ag from pure iron: One gram of an iron sample was dissolved in a mixture of hydrochloric and nitric acids. Palladium solution (3 mg as Pd), sulfuric acid and phosphoric acid were added to the solution and the solution was heated to generate fume of sulfuric acid. Au, Ag and Pd were reduced to convert to their metals with 3 g of ascorbic acid. After the metals were dissolved in a mixture of 1 ml of nitric acid and 0.2 ml of hydrochloric acid, the solution was exactly filled up to 10 ml with distilled water. Ten  $\mu\text{l}$  of the solution was injected into a graphite-tube furnace attached to atomic absorption spectrophotometer. Atomization conditions of Au and Ag were the same as the condition on the procedure for no separation of Au and

Ag.

Calibration curve was constructed using solution prepared by mixing of solution of Pd (3 mg of Pd) and solutions of Au and Ag. Nitric acid and hydrochloric acid were contained in this solution.

### 3. Results and Discussion

#### 3.1 Removal of carbon and sulfur blanks from accelerator for combustion

Blank on chemical analysis means signal intensity originated from the same element as analyte in an analytical sample. The element was mixed in each step on an analytical procedure as contaminant from a ceramic crucible, accelerator and oxygen for combustion in the case of determination of C and S by combustion/infrared absorption method. High blank value inhibited determination of trace elements, as signal of the analyte was not distinguished from overlapping signal of blank that fluctuated sensitively. Therefore, it is very important that blank value is decreased or removed on chemical analysis. Because, by decrease in analytical blank, detection limit of analyte becomes lower and reliability of determination of trace element becomes good.

There were large blanks of C and S in an accelerator. But it has not been almost reported<sup>21,22)</sup> that an accelerator was heated to decrease and remove those blanks.

##### 3.1.1 Removal of carbon blank

Carbon blank in an accelerator was removed according to the procedure described on [2.3.1 in 2.3 Analytical procedure]. In order to remove carbon blank in it, the relationship between heating temperature in a muffle furnace and carbon amount remained in it was examined. The results were shown in Fig. 1. In cases of non-heating (plotted at 293 K) and heating at 473 K, blank values of carbon were similar. Average of the blank values of the 6 determinations corresponded to

$2.10 \pm 0.387 \mu\text{g}$  of carbon. By heating at temperature from 473 to 873 K, carbon blank decreased rapidly. From 873 K to 1073 K, blank value of carbon became zero. When the accelerator was heated over 1173 K for 15 min, radio frequency power could not be supplied for combustion of it, because all of W and Sn as an accelerator were converted into  $\text{WO}_3$  and  $\text{SnO}_2$ , by oxidation, respectively. On this study, condition of heating at 1003 K for 15 min (alternately repeated heat and stir three times) was selected.

It was thought that most of carbon blank was contained in W of an accelerator. However, chemical form of the blank was not clear. Carbon blank was oxidized to  $\text{CO}_2$  together with oxidation of W that rapidly changed to tungsten trioxide by heating in a muffle furnace. Since C of carbon blank was evaporated as  $\text{CO}_2$  from the accelerator, carbon blank was removed from it. At that time, most of Sn as an accelerator remained as metal, because Sn as an accelerator was oxidized more slowly than W. Therefore, the remainder of Sn could was subjected to combustion by radio frequency power.

Trace amounts of carbon in pure irons were determined by use of an accelerator removed carbon blank. The relationship between sample mass (g) and amount of carbon ( $\mu\text{g}$ ) found in irons was shown in Fig. 2. The relation was linear. Equations of the straight lines were calculated by the least-squares method and shown in Table 1. The slopes of the lines corresponded to carbon content ( $\mu\text{g g}^{-1}$ ) in an analytical sample. As can be seen from equations in Table 1, the straight lines in Fig. 2 passed through the origin of the coordinate. This means that carbon blank was removed until it became nearly zero.

Really, when carbon in the accelerator that was previously heated at a muffle furnace was determined, it was shown that analytical values of carbon were always zero. Therefore, detection limit of carbon was defined as the lowest  $0.01 \mu\text{g g}^{-1}$  of a gauge equipped the analyzer.

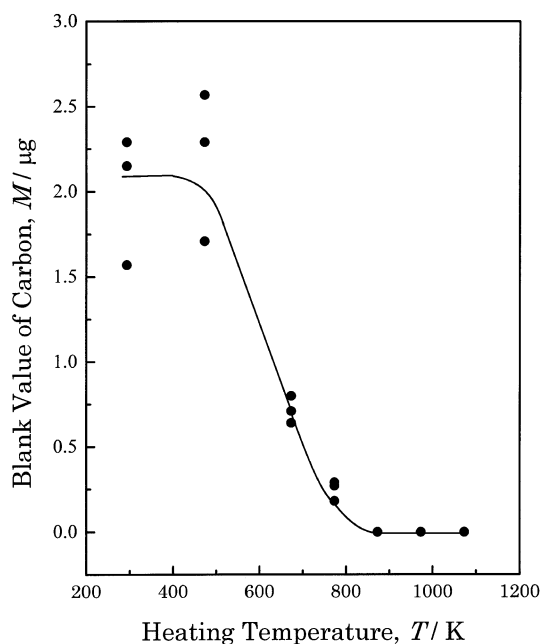


Fig. 1 Relationship between heating temperature and carbon amount in accelerator for combustion. Accelerator: Mixture of W 1.5 g and Sn 0.5 g Heating time: 15 min.

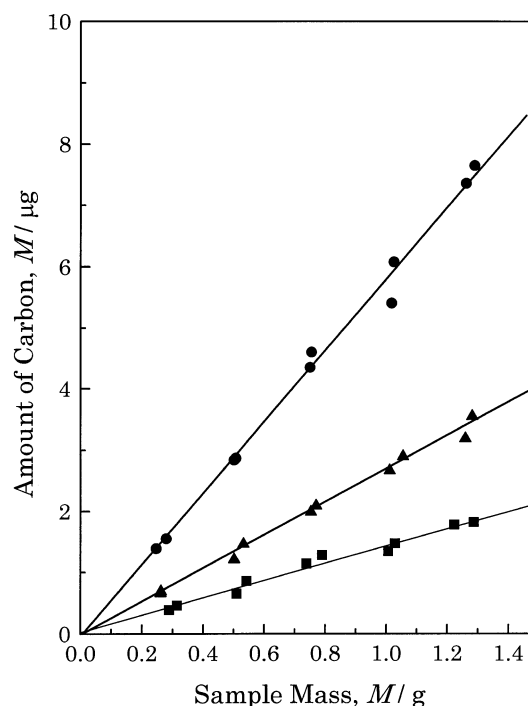


Fig. 2 Relationship between sample mass and amount of carbon found in high-purity iron and steel. Sample: ● JSS 1201-1, ▲ JSS 001-4, ■ A-Iron.

Table 1 Analytical results for carbon in pure iron.

Sample	C found + C blank found ( $\mu\text{g g}^{-1}$ ) ( $\mu\text{g}$ )		C found ( $\mu\text{g g}^{-1}$ )	Certified value ( $\mu\text{g g}^{-1}$ )
	With data shown in Fig. 2		With data shown in Fig. 3	
A-iron (High-purity electrolytic iron)	$Y = 1.42X + 0.02$		$1.45 \pm 0.11$	—
JSS 001-4 (Pure iron)	$Y = 2.70X - 0.03$		$2.64 \pm 0.12$	(2.5)*
JSS 1201-1 (Steel for determination of carbon)	$Y = 5.89X - 0.03$		$5.74 \pm 0.22$	5

(\*)\*: Non-certified value.

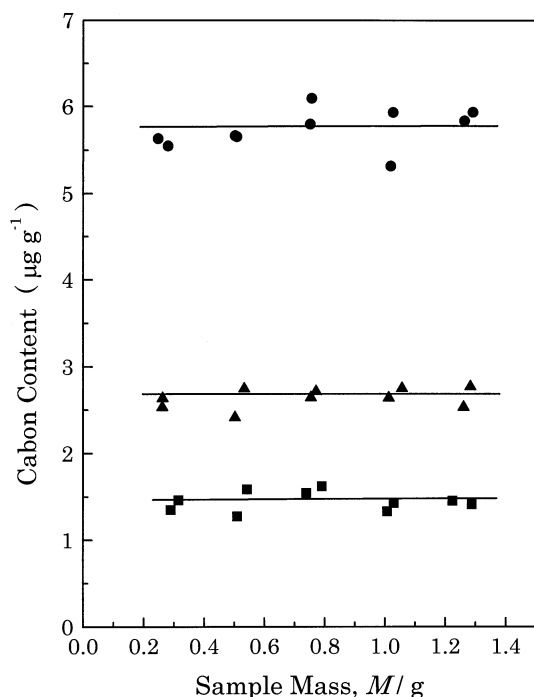


Fig. 3 Relationship between sample mass and carbon content found without subtraction of carbon blank. Sample: ● JSS1201-1, ▲ JSS 001-4, ■ A-Iron.

In order to evaluate optimal mass of an analytical sample, the relationships between sample mass (g) and contents of carbon ( $\mu\text{g g}^{-1}$ ) found in the irons were determined. The data were obtained by arrangement of data used in Fig. 2. They were illustrated in Fig. 3. The averages of the contents were shown in Table 1. As shown in Fig. 3, analytical values of each sample were stable in the range of 0.25 to 1.25 g of a sample. This means that the samples were sufficiently subjected to combustion and carbon in the sample was quantitatively converted to  $\text{CO}_2$  to be determined by infrared absorption method.

### 3.1.2 Decrease in sulfur blank

A similar treatment of removal of carbon blank in an accelerator for combustion was performed for decrease in sulfur blank in it as described on 2.3.1 in 2.3 Analytical procedure. When an accelerator for combustion was heated at 1003 K in a muffle furnace, the relationship between heating time and sulfur amount remained in it was examined. The result was

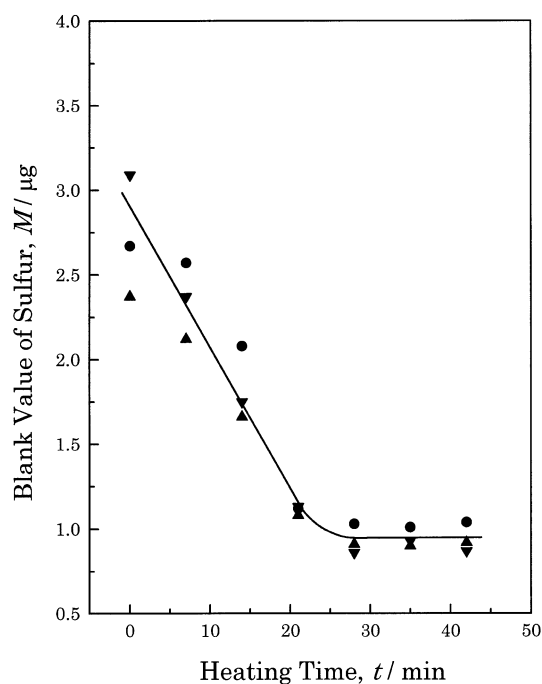


Fig. 4 Effects of heating time for accelerator on blank value of sulfur. Accelerator: Mixture of W 0.5 g and Sn 1.5 g. Heating temperature: 1003 K. A series of experiment: ● first, ▲ second, ▼ third.

shown in Fig. 4. Blank value of sulfur (2.3–3.2  $\mu\text{g}$  of sulfur) in an accelerator for combustion before heat was decreased with increasing heating time, and became very stable by heating for 28–42 min. Average of 9 values at 28, 35 and 42 min was  $0.94 \pm 0.07 \mu\text{g}$ . The relative standard deviation of the average was 7.4%. In this way, sulfur blank was finally remained. On this study, condition of heating at 1003 K for 28 min was selected. A method for elimination of sulfur blank was similar to it for removal of carbon blank. That is to say, sulfur blank was decreased by evaporation of  $\text{SO}_2$  that was generated by combustion of trace amount of sulfur compound as contamination in an accelerator (a mixture of 0.5 g of W and 1.5 g of Sn).

When detection limit of sulfur was defined as amount of sulfur corresponding to 3 times of standard deviation ( $0.07 \mu\text{g}$ ) of blank value of sulfur. It was  $0.2 \mu\text{g}$ . In the case of analysis of 1 g of a sample, the value corresponded to  $0.2 \mu\text{g g}^{-1}$  of sulfur content.

Trace amounts of sulfur in pure irons were determined by

Table 2 Analytical results for sulfur in pure iron.

Sample	S found + S blank found ( $\mu\text{g g}^{-1}$ ) ( $\mu\text{g}$ )		S found ( $\mu\text{g g}^{-1}$ )	Certified value ( $\mu\text{g g}^{-1}$ )
	With data shown in Fig. 5		With data shown in Fig. 6	
A-iron (High-purity electrolytic iron)	$Y = 0.71X + 1.03$		$0.71 \pm 0.15$ ( $0.69 \pm 0.06$ )*	—
Leco 501-078 (Low sulfur iron)	$Y = 1.06X + 1.03$		$1.06 \pm 0.13$ ( $1.04 \pm 0.09$ )*	—
JSS 001-4 (Pure iron)	$Y = 1.91X + 1.11$		$1.90 \pm 0.16$ ( $1.90 \pm 0.05$ )*	1.9

(\*) : In a case of rejection of data from 0.25 g of sample mass.

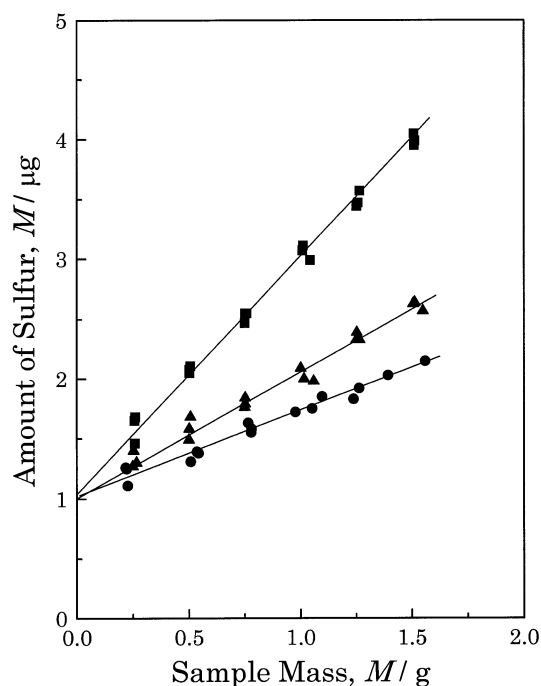


Fig. 5 Relationship between sample mass and amount of sulfur found in high-purity iron. Sample: ■ JSS 001-4, ▲ LECO 501-078, ● A-Iron.

use of an accelerator decreased sulfur blank. The relationship between sample mass (g) and amount of sulfur ( $\mu\text{g}$ ) found in irons was shown in Fig. 5. The relation was linear. Equations of the straight lines were calculated by the least-squares method and shown in Table 2. The slopes of the lines corresponded to sulfur content ( $\mu\text{g g}^{-1}$ ) in an analytical sample. As can be seen from equations in Table 2, the straight lines in Fig. 5 passed on the Y-axis (shown amount of sulfur) of the coordinate. This means that sulfur blank was decreased until it became stable, but it did not finally become zero.

In the same manner as Fig. 3, in order to evaluate optimal mass of an analytical sample, the relationships between sample mass (g) and contents of sulfur ( $\mu\text{g g}^{-1}$ ) found in the irons were determined. The data were obtained by arrangement of data used in Fig. 5. They were illustrated in Fig. 6. The averages of the contents were shown in Table 2. As shown in Fig. 6, analytical values of each sample were stable in the range of 0.5 to 1.25 g of a sample. However, the values of 0.25 g of the sample were not accurate and precise. It was

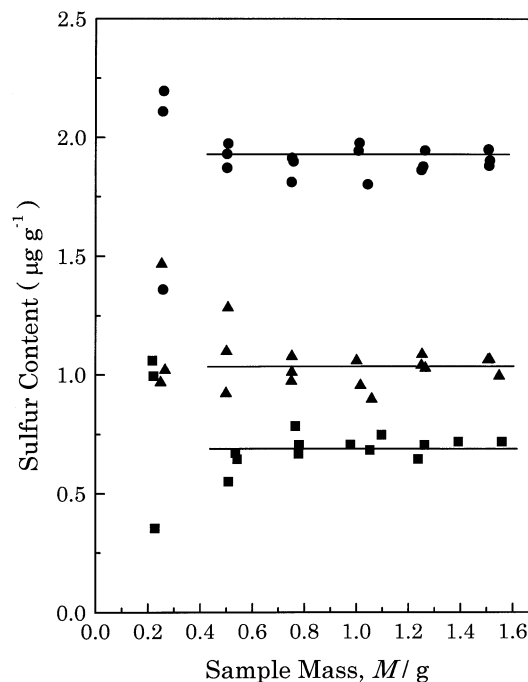


Fig. 6 Relationship between sample mass and sulfur content found with subtraction of sulfur blank. Sample: ● JSS 001-4, ▲ LECO 501-078, ■ A-Iron.

thought that analytical results were influenced by both fluctuation of sulfur blank remaining in the accelerator after heat and segregation of sulfur in small sample (0.25 g).

### 3.2 Determination of Sn by electrothermal atomic absorption spectrometry

Tin in pure irons was determined by electrothermal atomic absorption spectrometry with and without co-precipitation separation according to the procedure described on [2.3.2 in 2.3 Analytical procedure]. On the separation, metallic Pd was used as co-precipitant. Metallic Pd had been rarely used as co-precipitant. It was available as co-precipitant within a co-precipitation procedure and as chemical modifier when trace tin was determined by electrothermal atomic absorption spectrometry. Analytical results were shown in Table 3. By separation of tin from major component (iron), detection limit became lower than it without separation. The detection limit was defined as value corresponding to three times of standard deviation of blank values.

Table 3 Determination of tin in high purity iron by ET-AAS with and without separation of tin from major component (iron).

Sample	Sample taken, g	Sn found, $\mu\text{g g}^{-1}$		
		With separation	Without separation	
Pure iron (JSS 001-4)*	1.0	$0.29 \pm 0.00_1$ ( $n = 5$ )	0.3	0.4
	Limit of detection	0.02	0.3	

\*1: Japanese Iron and Steel Certified Reference Materials, Sn < 0.4  $\mu\text{g g}^{-1}$ .

Table 4 Determination of gold and silver in high purity iron by ET-AAS with and without separation from major component (iron).

Sample	Au found, $\mu\text{g g}^{-1}$		Ag found, $\mu\text{g g}^{-1}$	
	With separation	Without separation	With separation	Without separation
Low alloy steel (NIST SRM 2165)*	< 0.003 ( $n = 3$ )	< 0.03 ( $n = 3$ )	$1.85 \pm 0.073$ ( $n = 3$ )	$2.01 \pm 0.01$ ( $n = 3$ )
	Limit of detection	0.003	0.002	0.02

National Institute of Standards and Technology.

### 3.3 Determination of Au and Ag by electrothermal atomic absorption spectrometry

Gold and silver in pure irons were determined by electrothermal atomic absorption spectrometry with and without co-precipitation separation according to the procedure described on [2.3.3 in 2.3 Analytical procedure]. Metallic Pd as co-precipitant was the same as using for separation of tin. Similarly it was available as co-precipitant within a co-precipitation procedure and as chemical modifier when trace gold and silver was determined by electrothermal atomic absorption spectrometry. Analytical results were shown in Table 4. The detection limits of gold and silver with separation were one order lower than it without separation. Detection limit was defined as value corresponding to three times of standard deviation of blank values.

## 4. Conclusion

It is necessary for the determination of trace elements in a pure iron that the blank value during analytical procedure was removed or decreased to lower level of it, and the trace elements were chemically separated from the major component (iron). Therefore, for determination of trace C and S by combustion/infrared absorption method, C and S blanks in an accelerator for combustion were removed or decreased by heat it in ambient atmosphere. When trace Sn, Au and Ag

in pure iron were separated from major component (iron) by co-precipitation with metallic Pd, detection limits of these elements became lower than them without chemical separation.

## REFERENCES

- 1) S. Takaki: *Materia Japan* **33** (1994) 6-10 (in Japanese).
- 2) K. Abiko: *Materia Japan* **33** (1994) 11-15 (in Japanese).
- 3) T. Daicho and K. Abiko: *Materia Japan* **34** (1995) 279-281 (in Japanese).
- 4) K. Abiko: *Ultra High Purity Base Metals, Proc. UHPM-94*, ed. by K. Abiko, K. Hirokawa and S. Takaki (The Japan Institute on Metals, 1995) pp. 1-26.
- 5) K. Abiko: *phys. status solidi (a)* **160** (1997) 285-296.
- 6) S. Takaki and K. Abiko: *Handbook of High-Purification Technology*, Vol. 3, Manufacture Processes of Highly purified Products, by ed. H. Oya, (Fuji Techno-System, 1997) pp. 522-535 (in Japanese).
- 7) K. Abiko, T. Nakajima, N. Harima and S. Takaki: *phys. status solidi (a)* **167** (1998) 347-355.
- 8) S. Takaki and K. Abiko: *Mater. Trans., JIM* **41** (2000) 2-6.
- 9) K. Takada: *Materia Japan* **33** (1994) 84-87 (in Japanese).
- 10) K. Takada: *Materia Japan* **33** (1994) 307-312 (in Japanese).
- 11) K. Hirokawa, K. Takada, M. Saeki and Y. Nakamura: *Ultra High Purity Base Metals, Proc. of UHPM-94*, ed. by K. Abiko, K. Hirokawa S. Takaki (The Japan Institute of Metals, 1995) pp. 161-170.
- 12) K. Hirokawa, K. Takada, M. Saeki and Y. Nakamura: *Ultra High Purity Base Metals, Proc. of UHPM-94*, ed. by K. Abiko, K. Hirokawa S. Takaki (The Japan Institute of Metals, 1995) pp. 171-175.
- 13) K. Hirokawa, K. Takada, M. Saeki and Y. Nakamura: *Ultra High Purity Base Metals, Proc. of UHPM-94*, ed. by K. Abiko, K. Hirokawa S. Takaki (The Japan Institute of Metals, 1995) pp. 176-182.
- 14) K. Takada: *phys. status solidi (a)* **160** (1997) 561-565.
- 15) K. Takada, I. Inamoto and T. Okano: *Microchem. J.* **49** (1994) 291-297.
- 16) *JIS Handbook* 40, Analytical Methods of iron, steel, ferroalloy and ores, (Japanese Standard Association, 1998), (in Japanese).
- 17) *JIS Handbook* 41, Analytical Methods of nonferrous metals and alloys, (Japanese Standard Association, 1998), (in Japanese).
- 18) For example: On determination of C in iron, steel and unalloyed steel; ISO 9556 (1989), ISO/TR 15349-1 (1998), ISO 15349-2 (1999), ISO/TR 15349-3 (1998). On determination of S in iron and steel; ISO 4935 (1989).
- 19) "Annual Book of ASTM Standard 2000, Section 3, Metals Test Methods and Analytical Procedures", Volume 03.05, Analytical Chemistry for Ores, and Related Materials (I): E32 to E354.
- 20) "Annual Book of ASTM Standard 2000, Section 3, Metals Test Methods and Analytical Procedures", Volume 03.06, Analytical Chemistry for Ores, and Related Materials (II): E356 to latest.
- 21) T. Ashino, K. Takada, Y. Morimoto, H. Yasuhara, M. Kurosaki and K. Abiko: *Mater. Trans., JIM* **41** (2000) 47-52.
- 22) K. Takada, T. Ashino, Y. Morimoto, H. Yasuhara, M. Kurosaki and K. Abiko: *Mater. Trans., JIM* **41** (2000) 53-56.
- 23) K. Takada, Y. Morimoto, K. Yoshioka, Y. Murai and K. Abiko: *phys. status solidi (a)* **167** (1998) 389-397.
- 24) T. Takahari, K. Abiko, I. Ogawara, T. Imakita, S. Harimaya, Y. Inokuma, Y. Inamoto, Y. Ishibashi, K. Tanaka, S. Tomiyama, Y. Morimoto, K. Ban, T. Kikuchi, H. Okochi and K. Furuya: *TETSU-TO-HAGANE* **78** (1992) 774-781 (in Japanese).
- 25) T. Ashino and K. Takada: *J. Anal. At. Spectrom* **11** (1996) 577-583.
- 26) T. Itagaki, T. Ashino and K. Takada: *J. Anal. Chem.* **368** (2000) 344-349.