

Determination of Trace Amounts of Antimony and Boron in High-Purity Iron and Steel by Isotope Dilution/Inductively Coupled Plasma Mass Spectrometry*

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The highly sensitive and precise determination method for trace amounts of Sb and B in high-purity iron and steel has been established by the isotope dilution/inductively coupled plasma mass spectrometry. For the determination of Sb, the iron matrix was separated by anion-exchange chromatography using Dowex I-X8 in hydrofluoric acid solution, and the isotope ratio ($^{121}\text{Sb}/^{123}\text{Sb}$) of the $\text{HNO}_3/\text{H}_2\text{O}_2$ eluate was measured by ICP-MS. The isobaric interference of ^{123}Te was corrected by subtracting the intensity of ^{123}Te obtained by the relative intensity of ^{123}Te and ^{125}Te . For the determination of B, after the treatment of sulfuric acid-phosphoric acid fuming for the complete decomposition of boron nitride, B was separated by the anion-exchange chromatography using Amberlite IRA-743 at pH 8. The CyDTA was added to prevent the hydrolysis of iron. The isotope ratio ($^{11}\text{B}/^{10}\text{B}$) of the HCl eluate was measured by ICP-MS. By these methods, Sb and B in the range of $\mu\text{g/g}$ to sub- $\mu\text{g/g}$ could be determined with good precision. The limit of detection is 5.8 ng/g for Sb and 16 ng/g for B in steel.

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1. Introduction

It has become apparent that the chemical and physical properties of iron such as formability, toughness or corrosion resistance can be improved by reducing the amounts of impurities.¹⁻³⁾ Therefore, the precise determination of trace impurities is required in order to estimate the relationship between the material properties and the amounts of impurities.

Recently, inductively coupled plasma mass spectrometry (ICP-MS) that has high sensitivity for various elements has been employed to the trace analysis of iron and steel.^{4,5)} Furthermore, it enables very rapid isotope ratio determination, which in turn makes isotope dilution technique⁶⁻⁸⁾ possible. The isotope dilution technique is not affected by the recovery rate of analyte during the analytical process and by the drift of measurement of ICP-MS. It is suitable for the precise determination of trace elements in high-purity metals, and applied to the analysis of impurities in Cu^{9,10)} and Al.¹¹⁾

In the present study, a method for the highly sensitive and precise determination of trace amounts of Sb and B in high-purity iron and steel has been established by using the isotope dilution/ICP-MS after the removal of iron by ion exchange chromatography in order to decrease of matrix effects. Though Sb and B are difficult to be separated from the matrix quantitatively, this method is not affected by the recovery rate.

2. Experimental

2.1 Sample and reagent

Samples. JSS 002-1, and JSS 002-2 (Japanese iron and steel certified reference materials), NIST 365 (NIST standard reference material) and high-purity irons made by Kawasaki Steel Corp. (Sample A, B and C) were used as analytical samples.

Spike solutions. The enriched nuclide ^{123}Sb was purchased from Oak Ridge National Laboratory, USA and ^{10}B was from

CEA (Commissariat a L'Energie Atomique). The Sb spike solution was prepared by dissolving the ^{123}Sb (isotopic abundance 99.3%), in the mixture of hydrochloric acid and nitric acid. The B spike solution was prepared by dissolving the diboron trioxide powder containing 87.9% of ^{10}B in water.

Ion exchange resin. One mL of anion-exchange resin, Dowex I-X8, and cation-exchange resin, Dowex 50W-X8, were used for the analysis of Sb, and 1 mL of anion-exchange resin, Amberlite IRA-743, was used for the analysis of B. Each of them are packed in the mini-columns (content 2.5 mL) made of polypropylene.

Reagent. Hydrochloric acid, nitric acid, sulfuric acid, hydrofluoric acid, phosphoric acid and aqueous ammonia were electronic chemical grade, purchased from Kanto Chemical Co., Ltd., Japan. 1,2-Diaminocyclohexane-N, N, N', N'-tetraacetic acid (CyDTA) was purchased from Dojin Chemical Co., Ltd., Japan.

2.2 Operating condition for ICP and spectrometer

The ICP-MS used in this study was a Plasma Quad II plus (VG Elemental, Ltd., England). The conditions for ICP and mass spectrometer are shown in Table 1. The isotope ratio was calculated on the basis of the peak area.

2.3 Analytical procedure

The samples were decomposed and prepared based on the single test tube method¹²⁾ using Teflon (PFA) tubes for Sb

Table 1 Operating condition for ICP-MS.

ICP operation	Mass operation	
RF power	1.35 kW	Mass range 119.9–131.5 amu for Sb
Nebulizer gas flow	0.8 L/min	9.0–11.3 amu for B
Auxiliary gas flow	0.6 L/min	Number of channels 512
Plasma gas flow	12.5 L/min	Number of scan sweep 1500 times
		Dwell time 80 μs /channel

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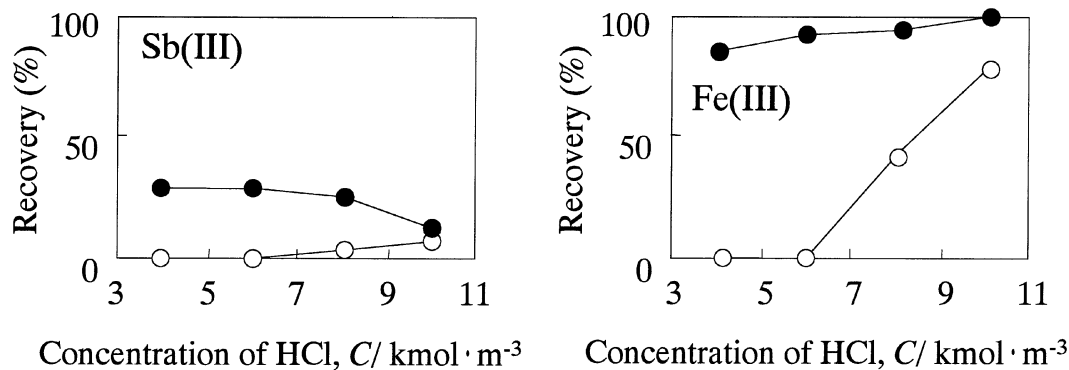


Fig. 1 Recovery of Sb and Fe by Dowex 50W-X8 cation-exchange resin(○) and Dowex 1-X8 anion-exchange resin(●) from HCl solutions.

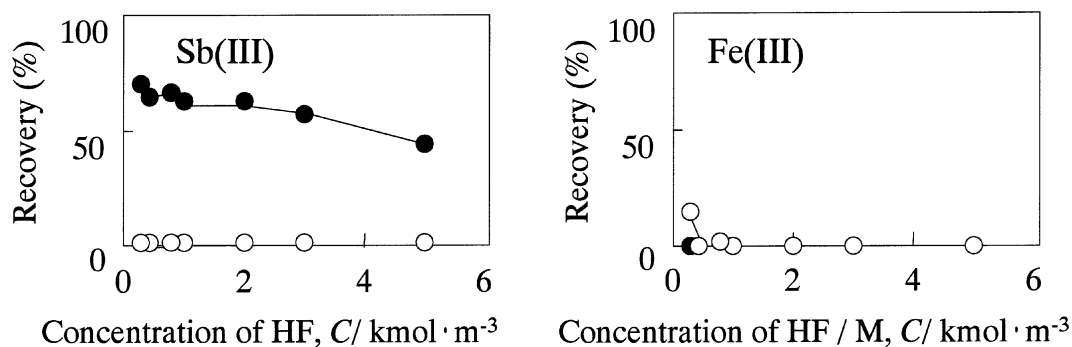


Fig. 2 Recovery of Sb and Fe by Dowex 50W-X8 cation-exchange resin(○) and Dowex 1-X8 anion-exchange resin(●) from HF solutions.

analysis and quartz tubes for B analysis.

Antimony analysis. A sample of 0.1 g was dissolved in a mixture of 2 mL of hydrofluoric acid (1 + 1) and 0.5 mL of hydrogen peroxide after the addition of ¹²³Sb as a spike. The sample solution was diluted with 6 mL of 1 M hydrofluoric acid, and was introduced to the column packed with 1 mL of Dowex I-X8. Sb was trapped on anion-exchange resin, and was eluted with 5 mL of the mixture of nitric acid and hydrogen peroxide. The isotope ratio (¹²¹Sb/¹²³Sb) of the eluate was measured by ICP-MS.

Boron analysis. After the addition of ¹⁰B as a spike, a sample was dissolved in 1 mL of the mixture of hydrochloric acid and nitric acid followed by the treatment of sulfuric acid-phosphoric acid fuming at 290°C for 30 min to decompose boron nitride in steel. Nine mL of 0.2 kmol·m⁻³ CyDTA in 5% NH₄OH solution was added to prevent the hydrolysis of iron. Four mL of aqueous ammonia were added to adjust the pH to 8.2. It was introduced to a column packed with 1 mL of Ambrelite IRA-743, and B was absorbed on the resin. After washing with 0.02 kmol·m⁻³ CyDTA to remove iron, B was eluted with 5 mL of 2 kmol·m⁻³ hydrochloric acid. The isotope ratio (¹¹B/¹⁰B) of the eluate was measured by ICP-MS.

3. Results and Discussion

3.1 Removal of matrix

In the trace analysis of solid sample, matrices should be removed to decrease various interferences, because co-existent matrix elements cause the spectral interference, mass discrimination, physical interference, and memory effect in the ICP-MS measurement.

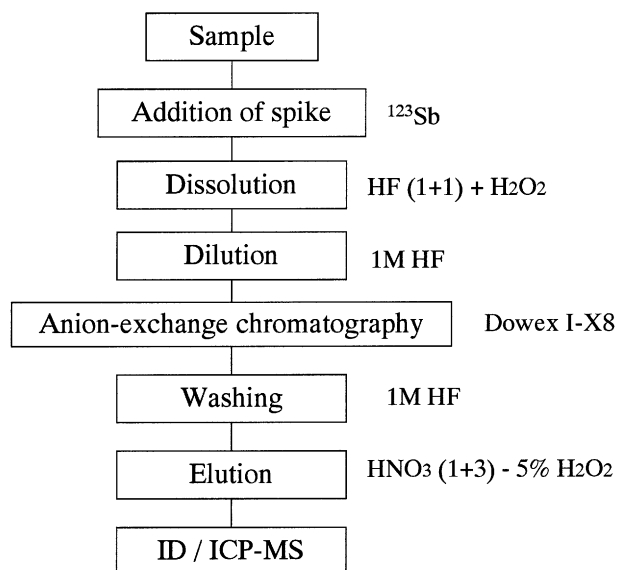


Fig. 3 Analytical scheme for Sb in steel.

For the trace analysis of Sb and B, ion exchange chromatography has been applied to remove the iron matrix and to pre-concentrate the analytes. Isotope dilution analysis is of great advantages when coupled with preconcentration technique, because there is no need to pay attention to the recovery rate in sample preparation.

Cation and anion-exchange chromatography is commonly used for chromatographic separation, and the both techniques can be applied to the separation of Sb from Fe. Figures 1 and 2 show the recovery of Sb and Fe by Dowex 50W-X8

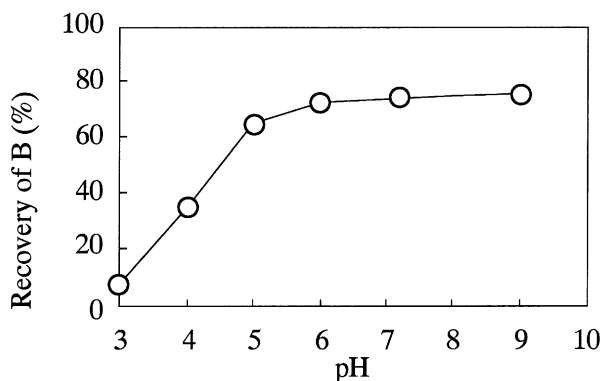


Fig. 4 Effect of pH on the recovery of B in the H_2SO_4 and H_3PO_4 solution B: $1\mu\text{g}$, Resin: 1 mL.

cation-exchange resin and Dowex I-X8 anion-exchange resin from hydrochloric acid and hydrofluoric acid. In all cases, Sb could not be separated quantitatively from iron matrix. Anion chromatographic separation in hydrofluoric acid was selected and applied for Sb analysis, because of their relatively highly recovery. The analytical scheme for Sb is shown in Fig. 3. According to this procedure, the recovery of Sb is about 60%.

Boron is known to partially exist as boron nitride in steel. A sample was dissolved in the mixture of hydrochloric acid and nitric acid followed by the treatment of sulfuric acid-phosphoric acid fuming to decompose the boron nitride completely. Boron was separated from iron matrix by anion-exchange chromatography using Amberlite IRA-743.^{13,14} This resin was known to adsorb B selectively in alkaline solution in the range of pH 7 to 12. In Fig. 4, the effect of pH on the adsorption yield of B in the presence of sulfate and phosphate is shown. Recoveries of B from the alkaline solution in the range of pH 7 to 9 were between 70 and 80%. Amberlite IRA-743 adsorbs anion, and it is speculated that the coexisting sulfate and phosphate ions are also adsorbed on this resin, which causes the decrease of the recovery of B. Because phosphate and sulfate interfered the recovery of B, the least amount of acids (1 mL of sulfuric acid and phosphoric acid) for the complete decomposition of boron nitride was used. When the pH of solution was higher than 10, the white precipitate that was assumed as ammonium hydrogen phosphate $[(\text{NH}_4)_2\text{HPO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4]$ appeared. By these results, the sample solution was adjusted to pH 8 by aqueous ammonia for chromatographic separation. The hydrolysis of Fe was avoided by addition of CyDTA. The present analytical scheme for B is shown in Fig. 5.

3.2 Optimization of isotope dilution analysis

In isotope dilution technique, the optimum amounts of spike to minimize the analytical error in the isotope ratio measurement, can be calculated. According to the proposal by Murozumi,¹⁵ the optimum amount of ^{123}Sb is about 6 times the amount of Sb in a sample, and that of ^{10}B is about equal to the amount of B in a sample. Table 2 shows the effect of the amount of the added spike (^{121}Sb) on the precision of the isotope ratio measurement. When the concentration of Sb was higher than 50 ng/mL, the variance of the isotope ratio $M_{121/123}$ was restrained below 0.5% in relative standard deviation (RSD). However, when the concentration of Sb was

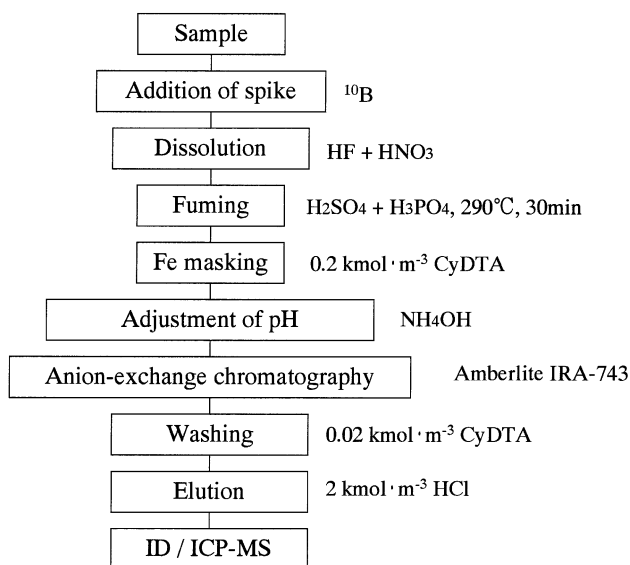


Fig. 5 Analytical scheme for B in steel.

Table 2 The effect of the amounts of the added spike (^{123}Sb) on the precision of the isotope ratio ($^{121}\text{Sb}/^{123}\text{Sb}$) measurement.

Concentration of Sb $\mu\text{g}\cdot\text{L}^{-1}$	10		20		30	
	$M_{121/123}$	RSD (%)	$M_{121/123}$	RSD (%)	$M_{121/123}$	RSD (%)
Amount of added ^{123}Sb						
[Sb] $\times 1$	0.4365	1.97	0.4306	0.32	0.4291	0.50
[Sb] $\times 5$	0.1231	0.66	0.1214	0.29	0.1218	0.38
[Sb] $\times 10$	0.0673	0.64	0.0666	0.22	0.0669	0.36

Table 3 Analytical precision of isotope ratio of Te.

Mass number	$(n = 10)$	
	Isotope ratio of $^{123}\text{Te}/^X\text{Te}$	
122	0.3581 ± 0.0032	
124	0.1851 ± 0.0018	
125	0.1241 ± 0.0009	
126	0.0446 ± 0.0004	
128	0.0255 ± 0.0002	
130	0.0228 ± 0.0003	

10 ng/mL, the spike of more than 5times the amount in sample was needed to obtain RSD below 1%. According to these results, the amount of spike should be 5times the amount of Sb in sample. In the case of B analysis, the good precision such as less than 1% in RSD in the isotope ratio measurement was obtained based on the same evaluation. The optimum amounts of ^{10}B were estimated to be equal to the amount of B in sample.

Using the quadrupole type ICP-MS, ^{123}Sb were is subject to the isobaric interference from ^{123}Te . The interference was corrected by subtracting the intensity of ^{123}Te calculated from the relative intensity of Te isotopes. Table 3 shows the analytical precision of isotope ratio of Te. Though the ratio of $^{123}\text{Te}/^{128}\text{Te}$ and $^{123}\text{Te}/^{130}\text{Te}$ was measured with good precision, ^{128}Te and ^{130}Te were interfered by ^{128}Xe and by ^{130}Ba and ^{130}Xe , respectively. It is concerned that Xe is contained in

Table 4 Analytical results of Sb in high-purity iron.

Sample	Certified and reference* value	Present method			
		With correction		Without correction	
		Mean	Precision (σ)	Mean	Precision (σ)
JSS 002-1	<1	0.032	0.006	0.032	0.006
Sample A	8*	7.78	0.011	7.77	0.013
Sample B	15*	15.22	0.085	15.20	0.087

 $(n = 5, \mu\text{g/g})$

*: Determined by flame atomic adsorption spectrometric method after extraction of antimony iodide by TOPO-4-methyl-2-pentanone

Table 5 Analytical results of B in iron and steel.

Sample	Certified and reference* value	Present method	
		$(n = 6, \mu\text{g/g})$	
		Mean	Precision (σ)
JSS 002-2	0.5	0.57	0.006
NIST 365	1.2	1.43	0.014
Sample C	55*	56.2	0.58

*: Determined by curcumin complex spectrophotometric method after chloroform extraction

Ar as contaminant, and Ba sometimes contaminates the sample solution from environment. Likewise, ^{122}Te is interfered by Sn, and ^{124}Te and ^{126}Te are interfered by Xe. Consequently, ^{123}Te were corrected using the isotope ratio of $^{123}\text{Te}/^{125}\text{Te}$.

3.3 Analysis of high-purity iron

Analytical results of Sb and B in high-purity iron are shown in Tables 4 and 5. In Table 4, the analytical values of Sb were in good agreement with the reference values which were determined by flame atomic absorption method after extraction of antimony iodide by tri-n-octylphosphine oxide (TOPO)-4-methyl-2-pentanone (MIBK). The analytical values of Sb with correction of interference of Te were slightly larger than those without correction, and the precision were slightly improved.

In Table 5, the analytical values of B were in good agreement with the certified values and reference value which were determined by curcumin complex spectrophotometric method after chloroform extraction. In these samples, Sample C contains 24 $\mu\text{g/g}$ of B as boron nitride. This result confirmed that boron nitride was decomposed completely by this procedure.

The relative standard deviation of these analytical values are almost less than 1%, and it is suggested that these procedures are suitable for the trace analysis of iron and steel with good precision.

The limit of detection for Sb and B was defined as the concentration equal to 3 times the standard deviation of the blank values. By these methods, the limit of detection were 5.8 ng/g for Sb and 16 ng/g for B in steel.

4. Conclusions

The highly sensitive and precise determination method for trace amount of Sb and B in high-purity iron and steel has been established by the isotope dilution/ICP-MS.

For the determination of Sb, the iron matrix was separated by anion-exchange chromatography using Dowex I-X8 in hydrofluoric acid solution, and the isotope ratio ($^{121}\text{Sb}/^{123}\text{Sb}$) of the $\text{HNO}_3/\text{H}_2\text{O}_2$ eluate was measured by ICP-MS. The isobaric interference of ^{123}Te was corrected by subtracting the intensity of ^{123}Te obtained by the relative intensity of ^{123}Te and ^{125}Te .

For the determination of B, after the treatment of sulfuric acid-phosphoric acid fuming for the complete decomposition of boron nitride, B was separated by the anion-exchange chromatography using Amberlite IRA-743 at pH 8. The CyDTA was added to prevent the hydrolysis of iron. The isotope ratio ($^{11}\text{B}/^{10}\text{B}$) of the HCl eluate was measured by ICP-MS.

By these methods, Sb and B in the range of $\mu\text{g/g}$ to sub- $\mu\text{g/g}$ were able to be determined with good precision.

The limit of detection is 5.8 ng/g for Sb and 16 ng/g for B in steel.

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