Determination of Boron in Steel by Isotope-Dilution Inductively Coupled Plasma Mass Spectrometry after Matrix Separation

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The concentration of B in steels is important due to its influence on mechanical properties of steel such as hardenability, hot workability, and creep resistance. An analytical method has been developed to determine B in steel samples by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). National Institute of Standard and Technology Standard Reference Material (NIST SRM) 348a was analyzed to validate the analytical method. The steel sample was digested in a centrifuge bottle with addition of aqua regia and ^{10}B spike isotope. Sample pH was then adjusted to higher than 10 to precipitate most matrix elements such as Fe, Cr, and Ni. After centrifugation, the supernatant solution was passed through a cation exchange column to enhance the matrix separation efficiency. B recovery efficiency was about 37%, while matrix removal efficiency was higher than 99.9% for major matrix elements. The isotope dilution method was used for quantification and the determined B concentration was in good agreement with the certified value.

Key Words : Boron, Steel, Isotope dilution, ICP-MS, Precipitation

Introduction

Minute quantities of boron are added to steel for case hardening by the nitriding process to form a boron nitride, and in other steels to increase strength and hardness penetration. About 30 μg/g of B in the steels is beneficial, because larger amounts of boron may cause difficulties in rolling or forging.[1] Such a strong effect of boron on the steel properties requires precise and accurate determination of the element at μg/g level.[2] Sah and Brown[3] published an excellent review article for the boron determination and its isotopic composition. They recommended that the plasma source mass spectrometry appeared to be the method of choice among the many analytical methods available today for the boron determination.

Inductively coupled plasma mass spectrometry (ICP-MS) has attracted widespread interest because of its analytical figures of merit such as the excellent power of detection and the ability to measure isotope ratios. ICP-MS has been employed for the determination of boron in geological,[4] biological,[5] and steel[6,7] samples. Despite such salient features, ICP-MS suffers from both spectral and non-spectral interferences in most applications. Since boron is a light element, the non-spectral interference or the matrix effect is very serious. Furthermore the two isotopes ^{10}B and ^{11}B experience somewhat different matrix effect causing deviation in the measured isotope ratios due to the presence of the matrix elements. Coedo *et al.*[7] used the isotope dilution (ID) method for the determination of B in iron and steel samples. They employed a three-step solvent extraction method with acetylacetone-chloroform for the separation of the Fe matrix, and claimed that the Fe matrix removal efficiency was better than 99.8%. The solvent extraction method also uses two evaporation steps to eliminate solvent remaining in the aqueous phase. Since boric acid is volatile, there is a

possibility of B analyte loss when an acidic sample solution is heated for the evaporation. For an accurate determination of B by the ID method, matrix elements have to be eliminated to the level that the matrix-induced mass bias effect on the measured B isotope ratios is negligible. Thus 99.8% Fe removal efficiency of the solvent extraction method may not be enough because the remaining 0.2% Fe in the sample may induce mass bias effect on the measured B isotope ratios.

In this work, instead of the solvent extraction method, a simple sample preparation method has been used which employs the precipitation and cation exchange for the matrix elimination. The sample preparation method utilizes that most boron species are anionic $B(OH)_4^-$ in a strongly-alkaline solution.[8] The matrix removal efficiency was better than 99.99% for Fe. The ID method was used for quantification and it provided accurate results even when the analyte recovery efficiency was low and non-quantitative.

Experimental Section

Instrumentation. The high-resolution ICP-MS instrument employed in this work was an Element (Finnigan MAT, Bremen, Germany). The instrument provides three fixed resolution settings ($m/\Delta m$ = 300, 3000 and 8000). All data were acquired in low-resolution mode ($m/\Delta m$ = 300). A special combination of sample introduction units was employed to lower the boron blank level. Micro-concentric nebulizer (MCN-100, CETAC, Omaha, NE, USA) was used at a free aspiration mode. Sample aerosols were carried into the plasma through a PFA (perfluoroalkoxy) spray chamber followed by a torch with a Sapphire injector. Details of the instrument components, operating conditions and data acquisition parameters are given in Table 1. For the estimation of the matrix separation efficiency, a simultaneous ICP-

Table 1. Operating conditions and data acquisition parameters of HR-ICP-MS

ICP-	
RF power, W	1200
Sample uptake rate, mL/min	0.3
Argon gas flow rates, L/min	
Coolant	13.3
Auxiliary	1.0
Carrier	1.2
Torch	HF-resistant torch with a separate Sapphire injector tube
Nebulizer	MCN-100 (M2E)
Spray chamber	HF-resistant PFA spray chamber
Sampler cone	Copper, 1.0 mm orifice diameter
Skimmer cone	Copper, 0.7 mm orifice diameter
Data acquisition	
No. of passes	1000
Mass window, %	5
Search window, %	100
Integration window, %	100
Samples per peak	200
Sample time, s	0.002

emission spectrometer (PolyScan 61E, Thermo Jarrell Ash, Franklin, MA, USA) was used to determine matrix concentrations in the prepared sample solutions. Details of operating conditions and instrument components are listed in Table 2.

Reagents and Materials. A stock standard solution (5 mg/g) of boron, the boron isotopic standard (SRM 951) and the enriched isotope ^{10}B (SRM 952) were purchased from National Institute of Standards and Technology (NIST, Gaithersberg, MD, USA). A working standard solution was prepared by serial dilution of the stock standard solution. The deionized water was obtained from a Mill-Q Element water purifier (Millipore, Bedford, MA, USA). The cation-exchange resin (AG 50W-X8, 100-200 mesh) and the column (Poly-Prep) were purchased from Bio-Rad Laboratories (Richmond, CA, USA). HNO_3 and HCl for sample digestion, and NH_4OH for pH adjustment were of electronic grade purchased from Dongwoo Pure Chemicals (Iksan, Korea). HF used for cleaning of PFA bottles was of electronic grade

Table 2. Operating conditions of TJA simultaneous ICP-emission spectrometer

ICP-	
RF generator	27.12 MHz free running type
RF power	950 W
Argon gas flow rates, L/min	
Coolant	13
Auxiliary	1.0
Carrier	0.8
Torch	TJA demountable
Nebulizer	Cross-flow
Spray chamber	TJA baffle type
Observation height	15 mm
Spectrometer	0.75 m vacuum polychromator (grating: 2400 grooves/mm)

bought from Korea Yamanaka Materials (Gongju, Korea).

Sample Preparation. NIST SRM348a steel samples were decomposed in centrifuge bottles. To about 0.1 g of the steel sample in each centrifuge bottle, 1 mL of aqua regia (0.25 mL HNO_3 + 0.75 mL HCl) was added together with an appropriate amount of ^{10}B spike isotope. In order to minimize analyte loss through the BCl_3 volatilization,[9] the centrifuge bottles were placed in a beaker filled with ice water during the acid digestion. The same centrifuge bottle was used for the weighing, spiking and acid digestion to prevent contamination from bottles. A group of three samples (about 0.1 g each) were weighed for replicate analyses. The centrifuge bottles, Poly-Prep columns and PFA bottles used for collecting final sample solutions through the cation-exchange resin were cleaned by soaking them with an acid mixture of 5 M HNO_3 and 3.5 M HF for a day followed by soaking them with the deionized water for a week.

In aqueous samples, boron is present as both the $B(OH)_3$ and the $B(OH)_4^-$. In strongly-alkaline solutions where pH is higher than 10, most boron species are anionic $B(OH)_4^-$. Utilizing this behavior, boron was separated from the matrix elements. 8 M ammonia solution was added drop by drop to the digested sample solution to adjust its pH to higher than 10. At such a highly-alkaline solution, most matrix elements such as Cr, Ni, Mn and Si were found to be coprecipitated with $Fe(OH)_3$. A significant amount of B analyte was also lost due to the coprecipitation, but some fraction of the analyte, enough for the ID analysis, remained in the alkaline solution as anions. Supernatant solution was then collected after centrifugation. In order to eliminate the matrix elements further, the sample solutions were passed through a column packed with AG 50W-X8 cation-exchange resin in the H^+ form (100-200 mesh) and collected in the PFA bottles for ID analysis.

Results and Discussion

Matrix Separation Efficiency. The matrix separation efficiency was investigated to ensure that most matrix elements were eliminated by the coprecipitation with $Fe(OH)_3$ followed by the cation exchange. In Table 3 are listed amounts ($\mu g/g$) of the matrix elements left in the solution prepared from the precipitation and centrifugation, and in the solution prepared further through the cation exchange. Table 3 shows that the matrix separation efficiency is better

Table 3. Matrix separation efficiency

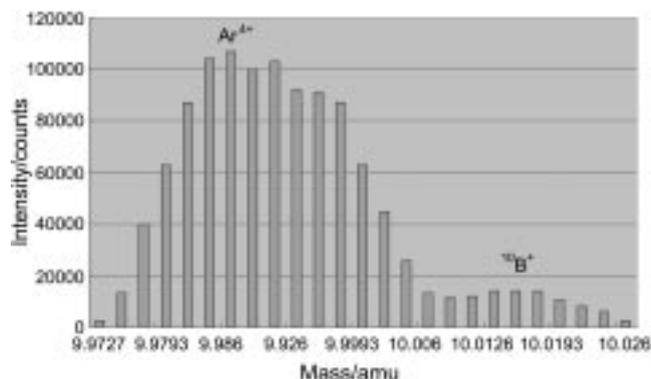| Separation step	Matrix concentration[a] ($\mu g/g$)					
	Fe	Cr	Ni	Mn	Si	Mo
Initial	3000	1500	1000	200	100	20
After precipitation	1.50	5.80	29.80	0.01	1.10	7.93
After cation exchange	0.01	0.67	0.05	0.01	0.69	7.97
Separation efficiency (%)	>99.99	99.96	99.99	99.99	99.32	60.15

[a]Uncertainty of determined concentration is 5%.

Figure 1. Mass spectrum showing slight overlapping of $^{40}Ar^{4+}$ peak onto $^{10}B^{+}$ peak.

than 99.9% for major matrix elements such as Fe, Cr, Ni and Mn. Mo is present as molybdate anions and is not effectively eliminated through the separation procedure. B recovery efficiency after the matrix separation was somewhat low and non-quantitative ($37 \pm 4\%$).

Spectral Interference. When a quadrupole ICP-MS instrument is used to measure the boron isotope ratio, the resolution is generally set to a high mode (0.6 amu separation) to prevent overlap of the ^{12}C low mass tail on ^{11}B. When the high-resolution ICP-MS instrument was used in this work, the interference from the ^{12}C low mass tail was not problematic at all, but a huge peak at around 9.99 amu interfered with the ^{10}B measurement. This peak was identified to be $^{40}Ar^{4+}$ and separation of this peak with ^{10}B required resolution of 448. In this work, boron isotope ratio was measured at resolution of 300, the two peaks ($^{40}Ar^{4+}$ and $^{10}B^{+}$) slightly overlapped as shown in Figure 1. However, the $^{40}Ar^{4+}$ peak did not affect the boron isotope ratio measurements because only 5% of the central peak area were integrated for the ratio measurements.

Matrix Effect. Matrix effects in ICP-MS are generally mass dependent due to the space charge effect.[10] Since boron is a light element, the matrix effect of any heavier element can be severe. Furthermore the two isotopes ^{10}B and ^{11}B experience somewhat different matrix effect causing deviation in the measured isotope ratios. The mass bias effect of added Fe on the measured B isotope ratio was investigated to find out a tolerable amount of matrix in the final sample solution after the matrix separation. Table 4 shows Fe matrix-induced mass bias effect for B isotope ratios measured using 100 ng/mL B isotopic standard solution. Table 4 shows that the B isotope ratios exhibit a noticeable change even at a matrix to analyte molar ratio of about 0.2 (100 ng/mL Fe). Thus it was necessary to ensure

Table 4. Fe matrix-induced mass bias for boron isotope ratio

Fe (ppb)	$^{10}B/^{11}B$ isotope ratio (100 ppb)
0	0.2484
100	0.2441
1000	0.2369
10000	0.2264

that matrix-induced mass bias effect was negligible by measuring B isotope ratios of the unspiked sample solutions together with those of the spiked sample solutions.

Memory Effect and Dead Time Effect. B is known to be one of the difficult elements to be determined due to a significant memory effect. Al-Ammar *et al*.[11] reported that a primary source of the memory effect was the volatilization of boric acid droplets in the spray chamber. In order to eliminate the memory effect, Vanderpool *et al*.[12] adjusted sample pH to about 10 by addition of ammonium hydroxide solution. A small amount of ammonia gas was also introduced with the nebulizer gas flow.[11] Sun *et al*.[13] added mannitol to the sample solutions to prevent B from binding to the spray chamber walls. In this work, sample solutions prepared from the matrix separation were already at pH higher than 10, and hence the memory effect from the volatile boric acid was not serious. 2% ammonium hydroxide solution was used as a washing solution between samples.

The mass bias effect on the measured B isotope ratios was corrected using NIST 951 isotopic standard solution. The dead time effect was automatically corrected with the instrument software. Besides the software correction, signal counts of the two isotopes were limited to between 100,000 and 200,000 to minimize the uncertainty from the dead time effect.

Isotope Dilution Method. All the analytical data reported here were quantified by following the ID protocol[14] proposed by NIST. The ID method is based on addition of a known amount of an enriched isotope to a sample. The altered isotope ratio of the mixture solution is measured by ICP-MS after equilibration of the spike isotope with the analyte in the sample. The analyte concentration is calculated inserting the measured ratio into the ID equation.[15] The spike concentration is determined by the reverse ID with a primary standard solution. When the reverse ID is used to calibrate the spike concentration, uncertainties from the spike enrichment, mass bias effect and dead time effect are minimized as long as isotope ratios of the spiked samples and the spiked primary standard are closely matched.[16,17]

Analysis of Steel Sample and Detection Limit. Three sample aliquots were separately spiked and analyzed using the ID method. Table 5 shows the determined concentrations along with the certified value for the NIST SRM348a steel sample. The measurement reproducibility (as relative standard

Table 5. Determined concentration of B in NIST SRM 348a steel sample

Spiked sample No.	Determined ($\mu g/g$)
1	58.0
2	57.1
3	58.4
Mean	57.8
Blank	0.4
Blank subtracted	57.4
Certified (uncertainty)	55(4)

deviation) of the determined concentrations is 1.2%. The determined concentration is in good agreement with the certified value within the uncertainty range. The blank concentration in Table 5 was determined by the ID analysis of the solution that was prepared using the same digestion and matrix separation procedure as the sample. Detection limit of the proposed analytical method was 0.15 μg/g. It was determined by calculating the concentration of the analyte that yielded a signal three times the standard deviation of the blank signal.

Conclusion

An analytical method has been successfully applied to the determination of B in a steel sample. Matrix-induced mass bias effect on the B isotope ratio was very severe due to the small mass and a large relative mass difference of the two B isotopes. For an accurate determination of B in steel samples, it is important to eliminate the matrix elements to the level that the matrix-induced mass bias effect is negligible. The simple sample preparation method of the precipitation followed by the cation exchange provided an excellent matrix separation efficiency of better than 99.9% for most matrix elements. The analyte recovery efficiency was poor, but the ID method enabled accurate determination of the analyte in spite of the low and non-quantitative recovery.

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