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Spectrophotometric Determination of Trace Amounts of Boron in High-Purity Iron and Ferroalloy after Chemical Separation

Ikuo Takahashi[1], Mikio Ishikuro[2], Kunio Takada[2], Kenji Abiko[2] and Kouzou Tsunoyama[1]

[1]*Kawasaki Steel Techno-research Corporation, Chiba 260-0835, Japan*
[2]*Institute for Materials Reseach, Tohoku University, Sendai 980-8577, Japan*

It is known that impurity elements in steel and other feeds exert an influence on the material characteristics. It is known that boron has a large influence on hardening and brittleness of iron even if a small amount of pole exists, and is requested a accurate quantitative analysis of with good repeatability. Boron is sensitively determined by spectrophotometry after color development with curcumin. However the blank value is high. Therefore, methanol and acids used for the analysis are refined, water is added in addition after color development, and the blank value has been decreased. As a result, the blank value decreased from 0.35 to 0.05 μg and the detection limit of boron became 0.01 ppm. Then, trace amount of boron in high purity electrolysis iron (mairon HP) became 0.24 ± 0.01 ppm by using this method. The separation of B from the matrix is possible hardly receiving the influence of the coexistence element. However, there are little examples of investigation on the recovery of boron by co-precipitation. Si was selected us an element to check the influence in this report. In addition, application of separation procedure to the Fe–Cr–Si alloy was performed. The decrease at the recovery of boron was admitted that the amount of Si in the solution exceeded 25 mg. Then, the Fe–Cr–Si alloy was taken, in which the amount of Si should not exceed 25 mg, and boron in the alloy was determined. As a result, it was possible to measure in the change coefficient (C.V) 3.1%.

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1. Introduction

It is well-known[1)] that the trace amount of boron in steels exerts a great influence on certain mechanical properties such as hardenability, hot work ability, *etc.* A recent development in purification of various kinds of metals such as iron and the other metals require to determine the low level impurities less than 1 ppm in these high purity metals. Inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and spectrophotometry have been generally used to determine trace impurities in high purity metals. However, ICP-MS and AAS are less sensitive for the determination of silicon, phosphorus and boron, and insufficient accuracy and low precision because of high exciting energy of spectra and spectral interferences of these elementsin these atomic spectrometry. However, the spectrophotometry is applicable with comparative high sensitivity.

In general, the limit of determination of trace boron in steel by JIS methods[2)] such as curcumin spectrophotometry after solvent extraction separation and methylene blue spectrophotometry show the limits of determination higher than 1 ppm. On the other hand the curcumin spectrophotometry after rapid chemical separation[3,4)] or combined with solvent extraction have made possible major advances in the limit of determination of trace boron determinations, which is less than 1 ppm. In particular, the curcumin spectrophotometry combined with rapid chemical separation is beneficial to simplify the procedure, and to reduce analytical time in trace boron determinations.

The study herein was investigated on the further improvements of detection limit, precision and accuracy for trace boron determinations in high-purity iron and ferroalloy by curcumin spectrophotometry combined with rapid chemical separation.

2. Experimental

2.1 Reagent

Special grades of acetic acid, sulfuric acid, phosphoric acid, sodium hydroxide, curcumin and methanol were used. Sodium hydroxide solution (0.8% (w/v)) was used for trapping trimetyl borate in a test tube and curcumin-acetic acid solution (0.15% (w/v)) was used as a colorimetric reagent of boron.

2.2 Procedure

Figure 1 shows the rapid chemical separation apparatus. Firstly, sample is dissolved in 20 mL of mixture of phosphoric acid, sulfuric acid and water mixtures in a quartz flask, then the solution is heated to fuming, followed by the addition of 35 mL methanol drop by drop to the solution with stirring on the hot plate at the temperature of 363 K. Trimethyl borate formed through the esterification of boric acid and methanol is evaporated and then is trapped into 7 mL of hot sodium hydroxide solution in a test tube to change into sodium borate and methanol saponification. The solution in the test tube are dried completely, and 1 mL of mixture of acetic acid and hydrochloric acid is added to the test tube for dissolving the residual salt. Finally, 5 mL of 0.15% curcumin-acetic acid solution and 4 mL of mixture of sulfuric acid and acetic acid mixtures are added to the residual salt solution in a test tube and the solution is allowed to stand for 20 minutes. Color development of boron is achieved on this stage. After the solution is diluted to 50 mL with methanol, the absorbance of sample solution at 550 nm is measured by spectrophotometry.

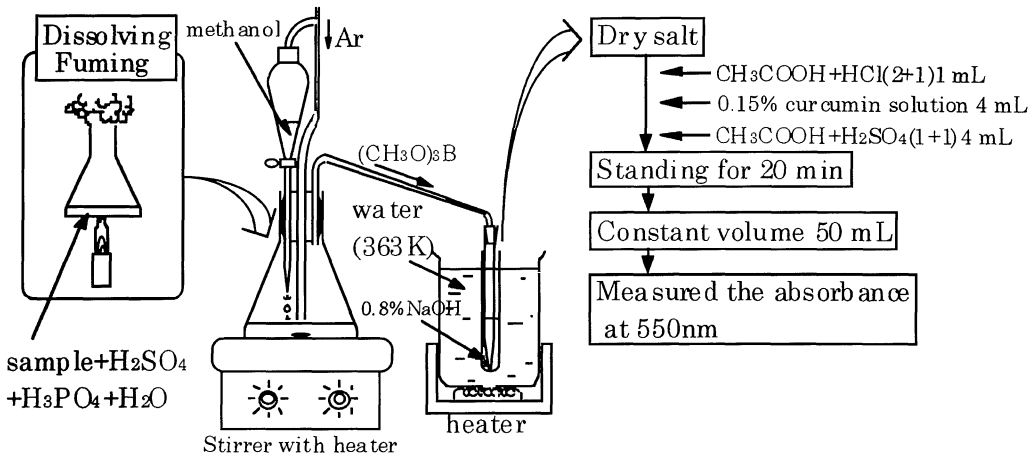

Fig. 1 Experimental procedure for the determination of trace boron.

3. Results and Discussion

3.1 The reduction in blank levels of boron in the reagents employed

In order to improve the limit of determination for trace boron determinations in high purity iron and ferroalloy, the blank levels of boron in various kinds of commercially available reagents: methanol, acetic acid, phosphoric acid and sulfuric acid were studied. Table 1 shows of the results of boron contents in various kinds of methanols with and without distillation. The boron contents were found to differ with the grades of methanol. Methanol C was the lowest boron contents among them. However distillation of methanol C is appeared to be ineffective for reducing the boron contents in it.

The results of the boron contents in two kinds of acetic acids and phosphoric acids are shown in Table 2, respectively. These acids showed almost the same levels of boron in them, and also showed that their distillation effects are insufficient for reducing the boron contents in them.

Finally, the results of boron contents in sulfuric acid were shown in Table 3. Hence, sulfuric acid was heated to fuming after hydrofluoric acid was added to the sulfuric acid. Table 3 shows the heat-fuming treatment of the acid mixture is found to be reduced the boron contents in the original acid to a small extent.

As described above, it was failed to observe any appreciable differences in the blank level of boron in commercial reagents such as methanol, acetic acid, phosphoric acid and sulfuric acid.

Table 1 The boron contents in commercial methanol with and without distillation.

Methanol	Without distillation	Without distillation
A	0.37_7	0.36_3
B	0.40_7	0.36_1
C	0.34_5	0.34_0

unit: μg/methanol 35 mL.

3.2 Effect of addition of water on the blank levels of boron determination

In order to decrease the blank levels of boron distilled water was added with methanol to the solution after color development. The effect of addition of water was studied on blank level of boron. The results are shown in Fig. 2. As shown in Fig. 2, open circles mean blank levels and open squares mean in case of addition of boron standard solution containing 1.00 μg boron. While closed circles show the absorbance differences between the corresponded open circles and squares, respectively. The absorbances at 550 nm due to the complex of curcumin and boron, which show wine red in color, was decreased with increasing the additions of water, and then attained its optimum effect above 5 mL of water additions. This is probably due to that not only the curcumin complex with boric acid but also the curcumin complex with sulfuric acid is formed in this matrix, in which the hydrolysis

Table 2 The boron content in two kinds of acetic acids and phosphoric acids.

(1) Acetic acid

Acetic acid	Without-distillation	Without distillation*
A	0.37_5	0.37_2
B	0.36_2	0.35_6

unit: μg/acetic acid 7.6 mL.

* Distillation: CH_3COOH 50 mL + H_3PO_4 5 mL $\longrightarrow_{397\,K}$ trap.

(2) Phosphoric acid

Phosphoric acid	Without distillation
A	0.31_6
B	0.29_7

unit: μg/phosphoric acid 7.5 mL.

Table 3 The boron contents in sulfuric acid.

Sample	Original	Heat-fuming treatment
Sulfuric acid	0.37_8	0.32_6

unit: μg/sulfuric acid 2 mL.

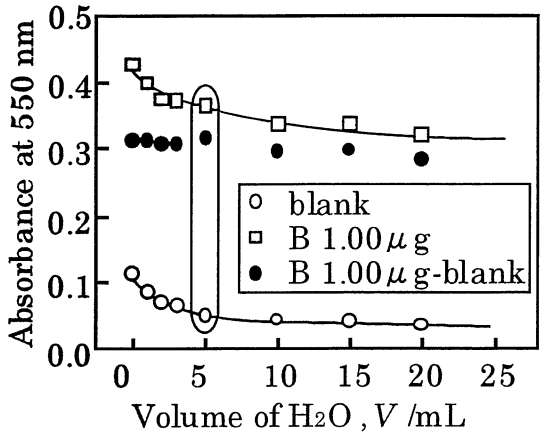

Fig. 2 Effect of addition of water on the absorbances of blank and boron standard solution containing of 1.00 μg boron.

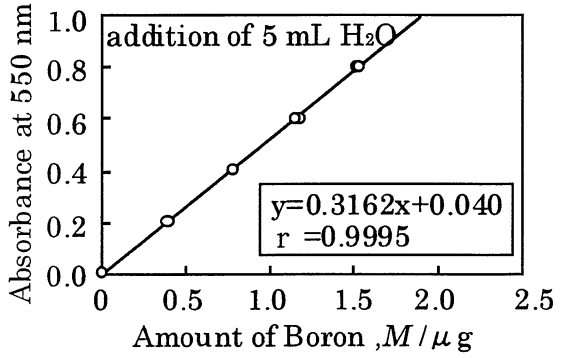

Fig. 3 The relation between the absorbance at 550 nm and boron contents with the addition of 5 mL H_2O.

of the curcumin complex with sulfuric acid is thought to be predominantly operational with the additions of water. Consequently, the blank levels were decreased from 7.4 to 1 μg/L and also the amount of scatter in measured values was reduced from 0.38 to 0.08 μg/L. On the basis of the results, it was possible to reduce the limits of determination of boron from 1.2 to 0.2 μg/L.

Figure 3 also shows the relation between the absorbances at 550 nm and boron contents in the matrix with the procedure of addition of 5 mL water. A linear correlation was found between the boron contents in the matrix and the absorbamces at 550 nm.

3.3 Determination of boron in high-purity electrolysis iron

It was carried out to determine the trace boron in high purity electrolysis iron. The results are summarized in Table 4. Average of boron content in high purity iron was 0.24 ppm when determination was repeated seven times by the optimized analytical conditions. The standard deviation was 0.01 ppm and the relative standard deviation was 4.8%.

3.4 Effect of silicon in the matrix on boron determinations

Generally, the rapid chemical separation is an excellent

Table 4 The results on determination of trace boron in high-purity electlysis iron.

Sample	Boron found (μg/g)	Number of runs	Relative standard deviation (%)
High-purity electrolysis iron Marion HP	$0.24_0(0.01_2*)$	7	4.8

* Standard deviation.

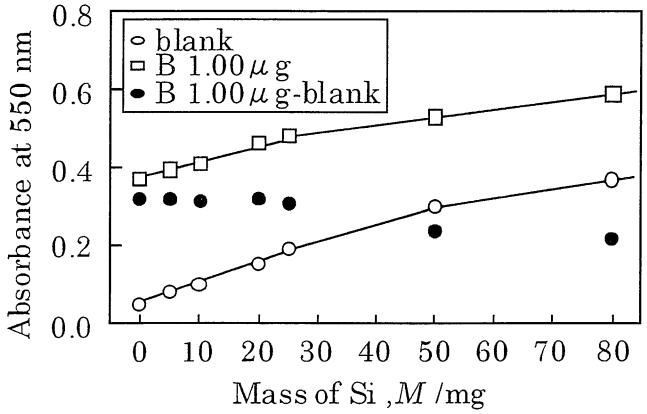

Fig. 4 Effect of Si on the absorbances at 550 nm due to boron complex.

method for liberating boron from the matrix without the interference of other species in the matrix. However, there are little informations on the sensitivity, precision and accuracy of trace boron determinations when a large amount of silicon coexisted in the matrix, in which silicon is precipitated during the heat-fuming treatment with sulfuric acid. The relation between the absorbances of boron and silicon contents in the matrix is shown in Fig. 4. The silicon solution was prepared by fusion of fused silica in sodium carbonate, followed by dissolving in water, and then a certain amount of silicon solution was added to a mixture of sulfuric acid, phosphoric acid and water. In Fig. 4, open circles are blank values and open squares show the absorbance of boron standard solution containing 1.00 μg boron added to the acid mixtures. Closed circles also show the absorbance differences between the corresponded open circles and squares, respectively. The blank values indicated comparatively higher levels due to that both silicon standard solution and sodium carbonate contained boron. However, both absorbances of blank and boron standard solution first raised with increasing the silicon contents in the matrix at a constant difference up to 25 mg of silicon additions. After passing 25 mg of silicon additions, the absorbance difference between standard solution and blank was varied and was tended to be smaller with increasing the silicon contents in the matrix. This is probably responsible for that insufficient boron liberation from matrix due to that silicon gel formation is taken place at the silicon contents above 25 mg. Thus, silicon gel formation is appeared to obstruct the boron liberation from the matrix or to inhibit the esterification between boron and methanol in the matrix. Table 5 shows the analytical results on boron contents and the blank in the presence of 20 mg silicon. The variation in pre-

Table 5 An alytical results on the boron contents in standard sulution containing 20 μg/L of boron and blank in the presence of 20 mg Si.

Sample	Boron found (μg/L)	Standard deviation (μg/L)	Recovery (%)
Blank	9.1_4	0.10_3	—
Standard solution Conaining 1.00 μg of boron	$20._1$	0.34_8	100.5

* Number of runs = 7.

Table 6 The composition of Fe–Cr–Si alloy.

Constituent	Certified value (mass%)	Estimated Uncertainty*
Boron	0.0017	0.0004
Carbon	0.043	0.002
Manganese	0.32	0.01
Phosphorus	0.026	0.002
Sulfur	0.002	0.001
Silicon	39.5	0.4
Copper	0.013	0.002
Nickel	0.20	0.03
Chromium	36.4	0.2
Vanadium	0.09	0.01
Aluminum	0.049	0.004
Titanium	0.40	0.01
Cobalt	0.034	0.003
Iron	23.2	0.2

* National Bureau of Standard SRM 689.

Table 7 Determination results of trace boron in Fe–Cr–Si alloy.

Sample	Boron found (μg/g)	Number of determination	Relative standard deviation (%)
Fe–Cr–Si alloy (NBS SRM 689)	13.91_7 (0.43_0)*	4	3.09

* Standard deviation.

cision in repeated blank runs was greater than that (1 μg/L) without silicon in the matrix. The recovery percentages of 1.00 μg boron are almost 100%. Consequently, it was found that the trace boron determinations could be operational when silicon contents in the matrix was less than 25 mg.

3.5 Determination of boron in ferroalloy

Boron in ferro-chrom-silicon alloy was determined. The composition of the alloy, NBS SRM689, is shown in Table 6. Its boron and silicon contents are 17 ppm and 40%, recpectively. The sample (50 mg) was weighed, implying that silicon content in the matrix was less than 25 mg, and was fused with mixture of 0.6 g of sodium carbonate and 1.2 g of sodium peroxide in a nickel crucible. After cooling, the sample salt was dissolved in hot water, following by the analytical procedure as described above. The analytical result is shown in Table 7. The boron determined was ranged within the certified value (17 ± 4 ppm), but the measurements were found to be performed within the relative standard deviation of 3.1% by controlling that the silicon content in the matrix was less than 25 mg.

4. Conclusion

(1) An attempt has been performed to decrease the limit of determination below 0.06 ppm in the trace boron determinations by rapid chemical separation spectrophotometry in this study. Consequently, the blank levels were decreased from 7.4 to 1 μg/L by adding 5 mL of water to the matrix, and then it was possible to reduce the limit of determination from 1.2 to 0.2 μg/L. Eventually, 0.24 ppm of boron in high purity electrolysis iron could be determined within the relative standard deviation of 4.8%.

(2) The influence of silicon contents on the trace boron determinations was studied, and then determined the boron contents in ferroalloy at the optimized conditions. As a result, the measurements were found to be performed within the relative standard deviation of 3.1% by controlling that the silicon content in the matrix was less than 25 mg.

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