Determination of Boron by Atomic Absorption Spectrometry with a Coated Graphite Furnace

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(Received July 15, 1996)

Abstract

Boron was determined by atomic absorption spectrometry with a coated graphite furnace. Pyrolytic graphite tubes were first coated with titanium carbide, and then further coated with tungsten carbide. A mixture of nitrates of strontium and nickel and citric acid was then added to a sample solution as a matrix modifier. Using this doubly coated tube and this matrix modifier, the determination of boron was successful with high sensitivity. No interference from metal nitrates and chlorides was observed. The sulfate interference could be removed by adding ammonium salt of EDTA.

Boron has been well known as one of the unamenable elements used for conventional atomic absorption spectrometry (AAS) with a graphite furnace, because a formation of refractory carbides with the carbon of the graphite tube before atomization occurs. The formation of refractory carbides causes remarkable reduction in both sensitivity and reproducibility; also memory peak arise due to the atomization of residual boron carbides formed during previous determinations.

Several approaches have appeared in the literature to resolve these problems. Some methods involve pre-coating the graphite tube with elements that tend to form more thermodynamically stable carbides than boron carbide and these coatings extend tube lifetime. Coatings with the elements such as tungsten1) and zirconium2),3) have been reported. Others have attempted to prevent the formation of refractory carbides by adding a suitable matrix modifier, which inhibits the reaction of boron carbide formation. Several matrix modifiers, such as salts of magnesium4)-7), calcium5),7),8), strontium6), barium9), nicke2)-4) and a titanium and ascorbic acid mixture10) have been proposed.

In a recent work11), we determined the boron by the use of a doubly coated graphite tube with titanium and tungsten carbides and by addition of a mixture of strontium and nickel nitrates and ascorbic acid as a matrix modifier. Using this doubly coated tube and this matrix modifier, the determination of boron was successful with higher sensitivity and good reproducibility. Ascorbic acid acted as reducing agent for analyte, but it also reduced copper(II) to copper(I) in the sample solution and copper(I) salt is

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precipitated. Therefore, when copper salt is present in the sample, the addition of ascorbic acid is difficult. In this case, citric acid also enhanced the sensitivity of atomic absorption of analyte similarly to ascorbic acid but it did not reduce the copper(II). In this study, using this doubly coated tube, a mixture of citric acid and metal nitrate was investigated as a matrix modifier in the determination of boron. The established method was applied to the determinations of boron in copper alloy without preliminary separation.

Experimental

Apparatus and reagents

A Hitachi Model GA-2B graphite-furnace atomizer was used with a Hitachi Model 180-30 atomic absorption spectrometer. A tube type coated graphite cell was used in an argon atmosphere. The signal was recorded with a Hitachi Model D-2500 chromato-integrator. A Hitachi boron hollow-cathode lamp was used as a radiation source. A deuterium-arc background correction was used throughout. Samples were deposited by using a Hitachi autosampler.

All of the solutions were prepared from analytical reagent-grade chemicals and deionized-distilled water, and stored in polyethylene bottles. A commercially available boron standard solution (Ishizu Seiyaku, Ltd., Japan) with a boron concentration of 1000 mg l^{-1} was diluted with deionized-distilled water to a working solution of 20 mg l^{-1}.

Tube coating procedure

The coating of pyrolytic graphite tubes with titanium carbide was treated in the following manner with reference to a method by Almedia and Seitz[12]. The tubes were immersed in liquid titanium tetrachloride under reduced pressure. A vacuum was applied until no more gas bubbles were observed to evolve from the graphite. The tubes were then placed in water for 24 h. After removal from the water the tubes were dried at room temperature for 1 h and at 100 ℃ for 3 h. The tubes were then placed in an atomizer and heated for 30 s at 100 ℃, at a heating rate of 20 ℃ s^{-1} to 1400 ℃ and for 12.5 s at 2900 ℃. This heating procedure in the atomizer must be repeated 3 times. This coating procedure should be repeated 2 times in order to obtain quantitative results.

Doubly treated tubes were prepared; the tubes coated with titanium were further coated with tungsten. The coating of tubes with tungsten carbides was treated with ammonium tungstate solution (2800 mg l^{-1}) involving similar procedure as that described above with titanium tetrachloride, except for placing the tubes in the water.

Procedure of sample analysis

A 10-μl sample solution was deposited in the center of a doubly coated graphite tube by an autosampler; it was then dried, ashed and atomized. Argon was used as a sheath gas at a flow rate of 2.0 l min^{-1} and a carrier gas (internal gas) at 0.1 l min^{-1}. The durations and temperatures were 30 s at 100 ℃ for drying, 30 s at 750 ℃ for ashing and 12.5 s at 2900 ℃ for atomization. In the presence of sulfate, the duration and temperature for ashing was 30 s at 1100 ℃. The absorbance signals during the atomization step were recorded at 249.8 nm (1.3 nm band width); the peak heights were taken as the analytical signals. The graphite tube was fired at the attainable maximum temperature (about 3000 ℃) for 3 s after measuring each sample, so as to clear any residue from the tube surface.

Results and Discussion

Effect of matrix modifier

It should be stressed that the absorbance values of boron were considerably low when the determination of boron was carried out without any matrix modifier. Here, the effects of alkaline earth metals, nickel and cobalt nitrates on the atomic absorption of analyte using a doubly coated tube were investigated for a salt concentration of 0.01 mol l^{-1}. Citric acid (10 g l^{-1}) was also added to the sample solution. Strontium nitrate and nickel nitrate gave the most effective enhancement of the sensitivity for the analytical signal. Strontium has been demonstrated to be useful as a matrix modifier for boron by Jiang et al.[6] and nickel by Liu et al.[3]. It has often been observed that the enhancement effect caused by the addition of a mixture of metal salts is more effective than that by the addition of each salt individually. In this boron determination, as shown in Fig. 1, the combined use of strontium and nickel nitrates resulted in a

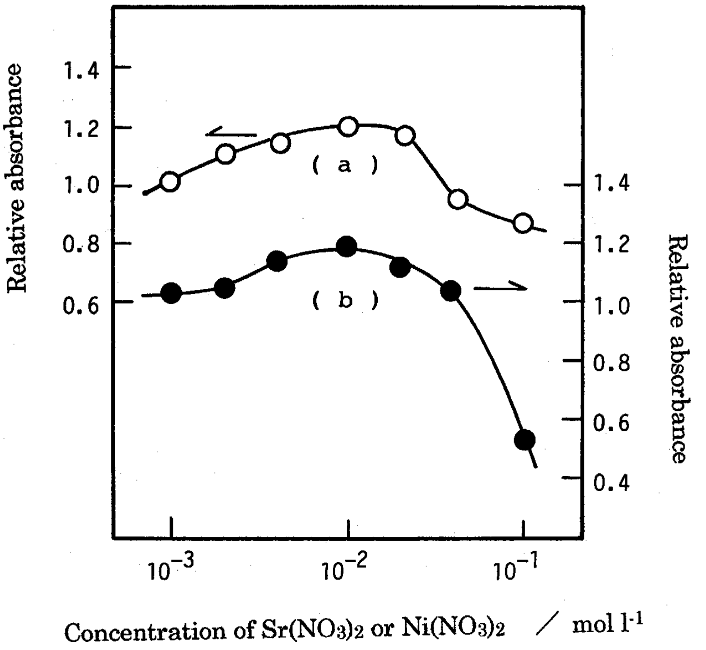

Fig. 1 Effect of (a) $Sr(NO_3)_2$ in the presence of 0.01 mol l^{-1} $Ni(NO_3)_2$ and (b) $Ni(NO_3)_2$ in the presence of 0.01 mol l^{-1} $Sr(NO_3)_2$ on the atomic absorption of boron (1.0 mg l^{-1}). All test solutions contain 10 g l^{-1} citric acid. The absorbance of each test solution is normalized by that of the respective solution containing (a) no $Sr(NO_3)_2$ or (b) no $Ni(NO_3)_2$.

synergistic effect on enhancing the sensitivity. The combination of 0.01 mol l^{-1} strontium nitrate and 0.01 mol l^{-1} nickel nitrate gave the highest analytical sensitivity.

Effect of citric acid

Since boron oxide has a large dissociation energy, the addition of an organic redaction agent has been useful for boron determination. In this study citric acid was used. The effect of concentration of citric acid on the analytical sensitivity of boron in the presence of 0.01 mol l^{-1} strontium nitrate and 0.01 mol l^{-1} nickel nitrate was investigated. As shown in Fig. 2, its concentration of 10.0 g l^{-1} shows the greatest enhancement effect on the sensitivity.

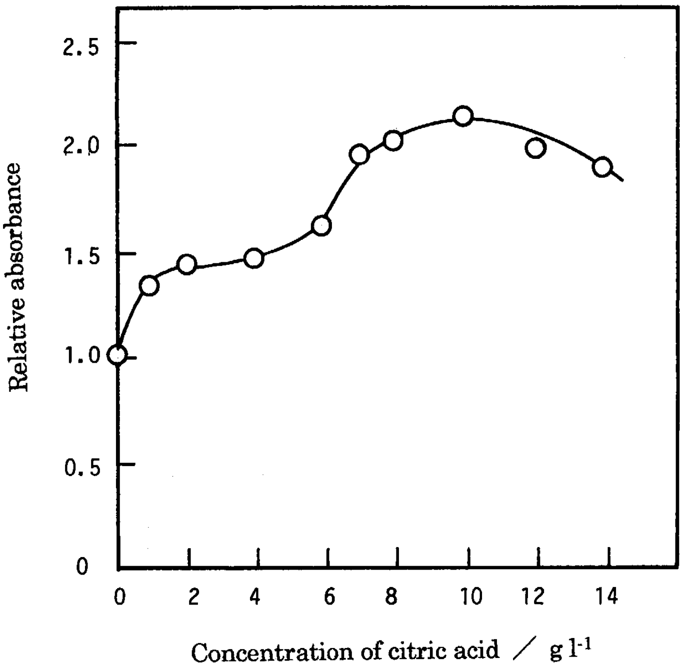

Fig. 2 Effect of citric acid on the atomic absorption of boron (1.0 mg l^{-1}) in the presence of 0.01 mol l^{-1} $Sr(NO_3)_2$ and 0.01 mol l^{-1} $Ni(NO_3)_2$ relative to absorbance without citric acid.

As a result, it is concluded that a mixture of 0.01 mol l^{-1} strontium nitrate, 0.01 mol l^{-1} nickel nitrate and 10.0 g l^{-1} citric acid is the best condition as a matrix modifier to enhance the analytical sensitivity of boron. Using a doubly coated tube and this matrix modifier, the calibration curve of boron was found to be liner up to at least 3.0 mg l^{-1}. The detection limit (3σ of the blank) and the relative standard deviation were estimated to be 0.048 mg l^{-1} and 3.5 % for 1.0 mg l^{-1} boron determination, respectively. This analytical sensitivity is almost the same as to that in the case of using ascorbic acid[11).

Effect of ashing temperature

Using a doubly coated tube and this matrix modifier, the effect of varying the ashing temperature on the atomic absorption signal of boron was investigated. As shown in plot (a) in Fig. 3, the maximum tolerable ashing temperature is about 800 ℃. Thus, 750 ℃ of ashing temperature was applied.

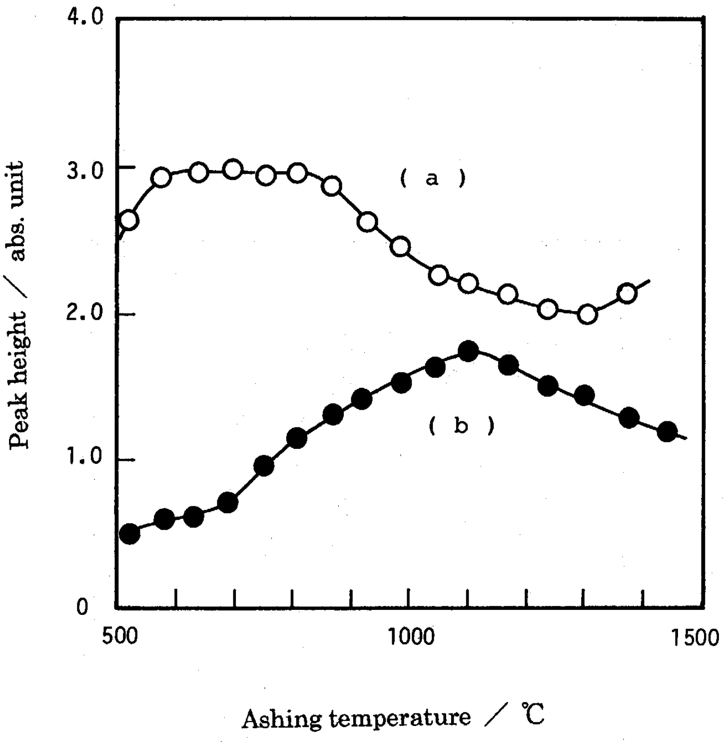

Fig. 3 Effect of ashing temperature on the atomic absorption of boron (1.0 mg l^{-1}) in the presence of (a) no sulfate and (b) 4×10^{-4} mol l^{-1} NiSO4. All test solutions contain 0.01 mol l^{-1} $Sr(NO_3)_2$, 0.01 mol l^{-1} $Ni(NO_3)_2$ and 10 g l^{-1} citric acid.

Effect of coexisting salts

The effects of coexisting nitrates and chlorides of sodium, potassium, magnesium, calcium, zinc, cobalt and copper(II) on the atomic absorption of boron were investigated. When the concentrations of nitrates and chlorides were less than 0.01 mol l^{-1}, the degree of interference was negligible. Above this concentration, the analytical signals were slightly suppressed. These phenomena were similar to those in the case of using ascorbic acid[11]. When ascorbic acid has been used, it has reduced copper(II) to copper(I) and the salt of copper(I) has been precipitated. However, in this case, copper(II) was not reduced and the precipitation of copper salt was not observed.

On the contrary, the interference from the coexisting sulfates was serious. This kind of sulfate interference may be interpreted in terms of the formation of volatile boron sulfide in the furnace during the preatomization stage followed by a thermal decomposition of coexisting sulfate. The sulfate interference may be affected by the ashing temperature. Therefore, the effect of varying the ashing temperature on the atomic absorption signal of boron in the presence of 4×10^{-4} mol l^{-1} nickel sulfate was investigated. As shown in plot (b) in Fig. 3, the maximum absorbance was observed at 1100 ℃. When the ashing was carried out at this temperature, the analytical sensitivity of boron was lower but the sulfate interference was suppressed. Hence, when a sample contained the sulfate, 1100 ℃ of ashing temperature was applied. The results obtained with the sulfates of ammonium, sodium and cobalt are shown in Fig. 4. In this case, 0.02 mol l^{-1} nickel nitrate was added in place of the mixture of strontium and nickel nitrates in order to avoid the precipitation of strontium sulfate. The results obtained with potassium sulfate was similar to that of sodium sulfate and those of zinc and copper sulfates were similar to that of cobalt salt.

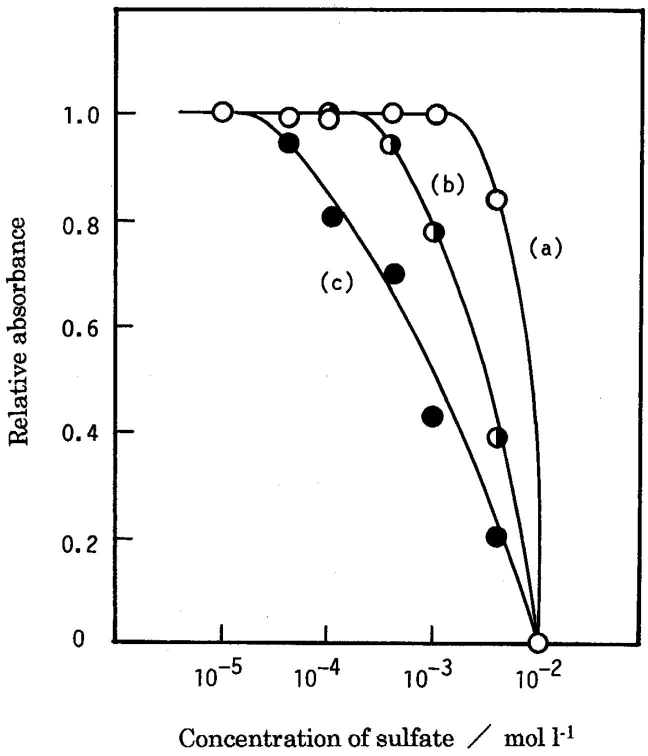

Fig. 4 Effect of some sulfates on the atomic absorption of boron (1.0 mg l^{-1}) in the presence of 0.02 mol l^{-1} $Ni(NO_3)_2$ and 10 g l^{-1} citric acid relative to absorbance without sulfate: (a), $(NH_4)_2SO_4$; (b), $CoSO_4$; (c), Na_2SO_4.

Because the interference from ammonium sulfate was negligible for its concentration less than 0.01 mol l^{-1}, removal of sulfate interference was investigated by adding EDTA ammonium salt. With EDTA, a small amount of ammonia was added. The coexisting sulfate may by eliminated from the furnace by the formation of ammonium sulfate, which decomposes at low temperature during ashing step. Because metal ions in the sample solution are masked by EDTA, the formation of metal sulfate of the inner surface of tube during the drying step may be prevented, and the elimination of ammonium sulfate from the furnace may be promoted. As the strontium

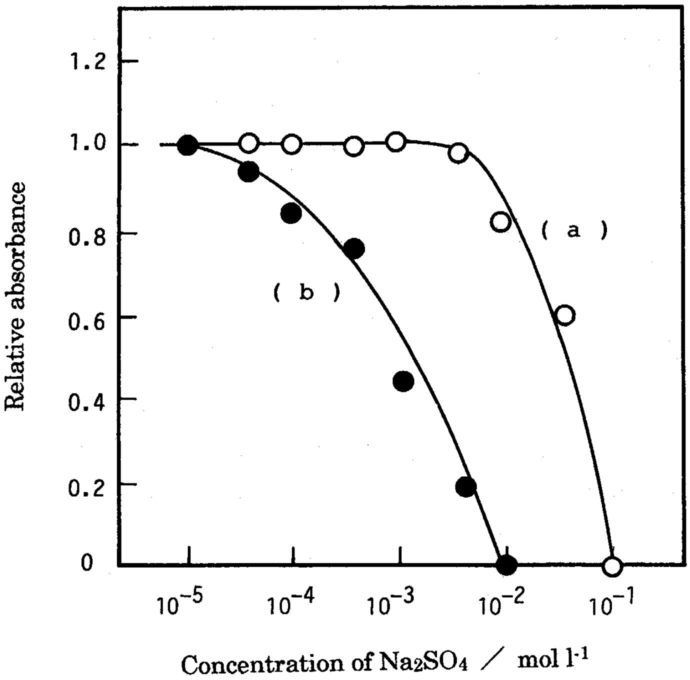

Fig. 5 Suppressing effect of ammonium salt of EDTA on Na_2SO_4 interference: (a) 0.04 mol l^{-1} $EDTA(NH_4)_4$, 0.5 mol l^{-1} NH_3, 0.01 mol l^{-1} $Sr(NO_3)_2$ and 0.01 mol l^{-1} $Ni(NO_3)_2$ added; (b) 0.02 mol l^{-1} $Ni(NO_3)_2$ added. Boron: 1.0 mg l^{-1}. All test solutions contain 10 g l^{-1} citric acid.

ions are masked by EDTA, the addition of strontium together with EDTA is permitted. Thus, by using the mixture of strontium and nickel nitrates as the matrix modifier the effects of ammonium-EDTA on the removal of sulfate interferences were investigated. Figure 5 shows the suppressing effect of EDTA ammonium salt on the interference from sodium sulfate. In the presence of EDTA and ammonia, the tolerable concentration of the coexisting sodium sulfate for boron is about 400-times greater than that in the absence of these reagents. In the presence of another sulfate, similar effects were observed.

Determination of boron in the metallic samples

The proposed method was applied to the determination of a trace amount of boron in metallic sample without preliminary separation. After the specimen was dissolved in a minimum volume of 6 mol l^{-1} hydrochloric acid, several drops of 30 % hydrogen peroxide were added by gentle heating; the solution was diluted to the volume with 0.1 mol l^{-1} hydrochloric acid. After an aliquot of sample solution was diluted to the volume with 0.01 mol l^{-1} strontium and nickel nitrates and 10 g l^{-1} citric acid, the atomic absorption signal of boron was measured. If the coexisting metal concentration is higher than 0.01 mol l^{-1}, the standard addition method is favorable.

The results for standard copper alloy samples are presented in Table 1, and show good agreement with the certified value and good recovery. Hence, the use of a graphite furnace doubly coated with titanium and tungsten carbides and a mixture of

Table 1 Determination of boron in a copper alloy sample

Sample	Sample taken/mg	B added /µg	B found[a] /µg	B in the sample[a]/%	Certified value/%	Recovery /%
MBH[b] C36XCN60 (Ni-Cu alloy)	252.5	–	25.8±2.0(7)	0.0102±0.0008	0.01	–
	252.5	12.5	38.7±2.5(5)	0.0154±0.0010	–	103

a) Mean and standard deviation with the number of determination of boron.

b) MBH: MBH Analytical Ltd. (UK).

strontium and nickel nitrates and citric acid as a matrix modifier was confirmed to be a suitable method for determining trace amounts of boron in metallic samples by AAS without requiring preliminary separation.

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