Determination of Boron by Graphite Furnace AAS:
Comparison of Different Modifiers

Application Note

Atomic Absorption

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Introduction

Various modifiers were investigated with respect to the best characteristic mass and the lowest memory effect for boron by graphite furnace spectrometry. Their influence on tube lifetime was also studied. The best results were obtained using a zirconium nitrate-nickel nitrate mixed modifier. This resulted in high sensitivity (characteristic mass 200 pg), a negligible memory effect and an increased tube life-time (about 200 atomization cycles at 2800 °C). The method was successfully applied to the determination of boron in river water, drinking water and sewage.

Boron is one of the "odd" elements in conventional graphite furnace atomic absorption spectrometry (GFAAS) because of the tendency of this element to form refractory carbides with the carbon of the graphite furnace before atomization occurs [1]. The problems associated with the formation of refractory carbides are loss of sensitivity, the occurrence of "memory peaks" due to the atomization of residual boron carbide formed during previous determinations, and the consequent use of high atomization temperatures to obtain a satisfactory vaporization of boron carbide (about 3000 °C in absence of a chemical modifier).

The combination of such a memory effect, which makes it necessary to apply 2-3 cleaning cycles between successive determinations, and the high atomization temperatures required to obtain a satisfactory vaporization of boron increases the analysis time and decreases the lifetime of graphite tubes (about 20 measurements for a pyrolytic coated graphite tube).

Several methods have been reported in the literature to remove all the problems mentioned above. Most of them attempt to prevent the formation of refractory carbides by means of a chemical modifier that inhibits this reaction, such as magnesium, calcium, strontium, barium, nickel, cerium and lanthanum or titanium and ascorbic acid mixtures [1,2,3,4,5].

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Some methods involve the pre-treatment of the graphite furnace with elements forming carbides that are more thermodynamically stable than boron carbide, such as tantalum, vanadium, zirconium.

In the present work, as an alternative to the time consuming soaking of graphite tubes with zirconium and the successive injection of the modifier in the so-treated tubes, various combinations of the best modifiers in terms of characteristic mass and memory effect and zirconium were injected before each atomization cycle in the untreated tube to increase the efficiency of boron vaporization.

Experimental

Instrumentation

An Agilent SpectrAA-250 Plus Atomic Absorption Spectrometer with a GTA-97 Graphite Tube Atomizer and a PSD-97 Programmable Sample Dispenser were used. A hollow cathode boron lamp was operated at 20 mA and the absorption was measured at 249.8 nm with a 0.2 nm slit bandwidth. A deuterium lamp was used to correct for background absorption. Pyrolytic coated partition graphite tubes were used. All data were plotted on an Epson LX-400 printer.

Reagents and Solutions

Stock solutions were prepared as in Table 1. The masses of the salts are chosen to give the indicated metal concentrations in g/L. The palladium solution was prepared by dissolving powder in concentrated nitric acid and diluted with Type I water. The solutions were stored in polyethylene bottles. Working boron solutions were prepared daily.

Table 1.   Preparation of Chemical Modifiers

Salt	Mass (g)	Conc. (g/L)	Medium
H_3BO_3	5.72	1	Type I water
$NiNO_3.6H_2O$	49.53	10	0.2% HNO_3
$CuSO_4.5H_2O$	39.32	10	0.2% HNO_3
$LaCl_3.7H_2O$	133.68	50	0.2% HNO_3
$Mg(NO_3)_2.6H_2O$	527.35	50	0.2% HNO_3
$Ca(NO_3)_2.4H_2O$	294.66	50	0.2% HNO_3
$SrCO_3$	84.25	50	10% HNO_3
$Ba(OH)_2$	12.48	10	Type I water
$Zr(NO_3)_4.5H_2O$	4.71	1	Type I water
Pd	10.00	10	

Results and Discussion

A chemical modifier is required for the determination of boron. Otherwise, poor sensitivity and very broad analytical peaks are obtained.

Elements such as calcium, magnesium, strontium and barium and their mixtures increase the efficiency of boron vaporization because of the formation of their respective borides, which are more volatile than boron carbides. Lanthanum can also provide a signal enhancement for boron [1].

Large amounts of lanthanum (100 µg) are necessary to obtain the best sensitivity for boron. This causes severe corrosion of tubes and platforms, and the analytically useful lifetime of the furnace was reduced to less than 50 determinations. In previous work [1] it has been shown that this phenomenon is due to excessive intercalation, which causes layer swelling and exfoliation of the lamellar pyrolytic graphite.

A number of modifiers were investigated in this study to find out which gave the best sensitivity for boron. Nickel and palladium were found to be more effective than the others [1,2].

The graphite furnace temperature is summarized in Table 2.

Table 2.   Graphite Furnace Temperature Program for the Determination of Boron

Step no.	Temp (C)	Time (sec)	Gas flow	Gas type (L/min^{-1})	Read command
1	85	5	3	NORMAL	NO
2	95	50	3	NORMAL	NO
3	120	20	3	NORMAL	NO
4	120	10	3	NORMAL	NO
5	1000	10	3	NORMAL	NO
6	1000	10	3	NORMAL	NO
7	100	18	3	NORMAL	NO
8	100	2	0	NORMAL	NO
9	2800	1.4	0	NORMAL	YES
10	2800	5	0	NORMAL	YES
11	2800	5	3	NORMAL	NO

The analytical peaks can be measured in both peak area and peak height. Peak height does not necessarily reflect atomization efficiency. Characteristic mass values; for boron under the effect of various modifiers are summarized in Table 3; it can be seen that, of all the investigated modifiers, nickel gives the best results both in absorbance and in integrated absorbance.

Table 3.   *Effect of Modifiers on Sensitivity and Memory*

Modifier	Peak height (A)	ABS (sec)	Characteristic mass (pg)	Memory effect
No modifier	0.003	0.006	24000	* * * * *
Mg	0.025	0.109	1615	* * *
Ca	0.111	0.467	377	* *
Sr	0.059	0.248	710	* *
Ba	0.027	0.119	1479	* * *
Ni	0.152	0.579	304	* *
Pd	0.053	0.220	800	* *
Cu	0.017	0.069	2550	* * *
La	0.081	0.378	466	* * * * *

* The characteristic mass is defined as the mass of analyte in picograms required to give an integrated absorbance signal of 0.0044 absorbance seconds

* The relative amount of memory effect is shown by "*"

Soaking of graphite tubes with zirconium solutions in combination with the use of nickel as modifier was found to improve the performance for the determination of boron1. Pre-treatment of graphite tubes with zirconium is time-consuming. So, different combinations of zirconium and a second modifier were pre-injected in the graphite furnace before each atomization cycle. The results obtained using different zirconium-modifier combinations are summarized in Table 4, expressed in terms of characteristic mass and memory effect. From Table 4 it can be seen that the best results were obtained using a combination of nickel nitrate and zirconium nitrate. Pre-treatment of graphite furnaces with zirconium and use of nickel as chemical modifier, as in the above mentioned work, gave results similar to that obtained after pre-injection of the mixed modifier zirconium nitrate-nickel nitrate in the untreated tube, for both characteristic mass and memory effect.

Table 4.   *Sensitivity Obtained with 20 µL of the Modifier having the Zr Concentration Equal to 1000 mg/L and the Concentration of the Other Component of the Mixture Equal to 3000 mg/L*

Modifier	Characteristic mass (pg)	Memory effect
Ca	220	NONE
Sr	280	NONE
Ni	200	NONE

There are two reasons why the combination of the two modifiers gives the substantial improvement seen:

1. Boron is easily vaporized as nickel boride, thus reducing the tendency of boron to react with the carbon surface of graphite tubes.

2. Zirconium forms a very stable carbide on the carbon surface and reduces the boron-carbon interaction (the B - C bond strength is 448 kJmol^{-1}, much smaller than the C - Zr bond strength, which is 561 kJmol^{-1}) [1].

The combination of modifiers above mentioned was applied to the determination of boron in river water, drinking water and in sewage. The samples were collected in polyethylene bottles, filtered and acidified with nitric acid to pH <2.

The analytical conditions were as indicated above and the analytical results are summarized in Table 5. In no instance was a matrix effect and a memory effect observed, and hence the standard addition method was not required. The procedure gave a high recovery of boron, as shown by data measured by adding known amounts of boron to the real samples and listed in Table 5.

Table 5.   *Determination of B in Water Samples*

Sample		CONC. (mg/L^{-1})	Recovery (%)	Method (mg/L^{-1})
Sewage	1	2.42 ± 0.05	95 ± 3	2.35 ± 0.06
	2	1.70 ± 0.03		1.65 ± 0.06
	3	0.89 ± 0.02		0.90 ± 0.03
	4	0.92 ± 0.03		0.93 ± 0.04
River water	1	0.32 ± 0.02	106 ± 5	0.30 ± 0.04
	2	0.34 ± 0.03		0.39 ± 0.03
Drinking water	1	0.12 ± 0.02	93 ± 6	0.12 ± 0.01

* Values reported are mean value of six determinations ± standard deviation

* Value for drinking water obtained after preconcentration of samples

To confirm the accuracy of the proposed method, the samples were analyzed by spectrophotometry as an alternative technique (reaction with carminic acid in concentrated sulfuric acid). The results showed very good agreement with those obtained by GFAAS (Table 5). The precision of the method (mean of six values between batches, expressed as relative standard deviation) was 1.9% and 1.2% for 0.9 and 2.0 mg/L^{-1} of B, respectively. The detection limit was calculated as 0.06 mg/L^{-1} and the determination limit was 0.18 mg/L^{-1}.

Conclusion

The proposed method for the determination of boron by the combination of zirconium nitrate and nickel nitrate as modifiers has advantages over the methods reported in the literature. Advantages include increased sensitivity, shorter analysis time, no memory effect, longer lifetime of the graphite tube and no pre-treatment of the graphite tube.

The method is suited for the determination of boron in river water, drinking water and sewage samples. It was shown that it is not necessary to use the standard addition method, which could be of interest for the routine analysis of such samples.

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