

1-1-2001

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SARICA, DENİZ YURTSEVER and ERTAŞ, NUSRET (2001) "Flow Injection Analysis for Boron Determination by Using Methyl Borate Generation and Flame Atomic Emission Spectrometry," *Turkish Journal of Chemistry*. Vol. 25: No. 3, Article 7. Available at: <https://journals.tubitak.gov.tr/chem/vol25/iss3/7>

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Flow Injection Analysis for Boron Determination by Using Methyl Borate Generation and Flame Atomic Emission Spectrometry

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Received 01.08.2000

Boron is one of the least sensitive elements in atomic emission spectrometry. As various refractory substances interfere in the analysis and because of the low sensitivity, sample enrichment and the separation of the interfering matrix is needed. Methyl borate has many advantages because of its simple generation conditions and its stability in the absence of moisture. New procedures for the generation of methyl borate without using external heating have also been investigated to produce a more rapid determination of boron.

The on-line combination of flow injection analysis using methyl borate generation with flame atomic emission spectrometry as the detector is proposed to provide sufficient enrichment factors in order to determine boron in different matrices.

In order to obtain as much moisture-free medium as possible, all standard solutions were prepared in 60% H₂SO₄ (v/v) according to the experimental results. The effect of Ar flow rate, peristaltic pump rate, size of the tubings used, and length of the mixing coil to the emission signal were all studied. Furthermore, the design of the gas liquid separator, and several ways to transfer the signal to AES were also examined in detail. A linear calibration graph was obtained between 10 and 2000 µg/mL with the equation $y = 0.1105X - 1.496$. The detection limit of the method was calculated as (3S) 2.96 µg/mL or 0.74 µg B.

Key Words: Boron, AES, Methyl borate formation, flow injection.

Introduction

The determination of boron has become a task of growing interest in different fields of analytical applications, such as environmental technology, industrial hygiene, and agriculture, because of the increasing use of boron compounds in metallurgy, microelectronics, glass products, fertilizers, and even cosmetics¹. From these sources, boron and its compounds might get into the environment. According to the literature, the toxicity

of boron and its compounds is not very pronounced, but the assimilation of its compounds may result in a cumulative toxic effect on human health². Boron may increase the serum concentration of some hormones³ that participate in the calcium, magnesium and phosphate metabolism⁴. On the other hand, boron is an essential trace element for many plants, and apparently controls their calcium metabolism; in the case of boron deficiency, the pectin lipids ratio is shifted in favor of the pectin⁵. A disturbance of the nucleic acid metabolism of plants, resulting in growth disturbances, has also been reported in cases of boron deficiency⁵, and hence, boron is added to many fertilizers.

For boron determination, several techniques have previously been used, such as UV-Visible molecular absorption spectrometry^{6,7}, and DC plasma optical emission spectrometry⁸. However, these are more complex and slower methods than those based on atomic absorption spectrometry. The determination of boron by electrothermal atomic absorption spectrometry (ET-AAS) is one of the most difficult tasks in analytical practice¹. Boron forms oxides, nitrides and carbides of high thermal stability, both in the condensed phase and in the gas phase. For that reason, boron determination by AES may be carried out either using more energetic excitation sources (such as DCP or ICP plasmas) or employing boron oxide as the analytical species to be measured⁹.

ICP-MS has outperformed all previous analytical methods for trace element determination for B¹⁰. Nevertheless, the conventional flame atomic emission and flame atomic absorption methods have limited application in the determination of boron owing to their poor sensitivity and a large number of interferences.

Boron determination by AES, measuring boron oxide emission, has been performed using different types of flames. However, these methods in general have low sensitivities and, occasionally, interference problems¹¹. As a result, several separation (and/or preconcentration)-AES combined techniques, both separation and concentration methods, i.e., distillation of methyl borate, extraction of the ester formed between the boric acid and 1,3-diols in organic solvents, overcome some of these problems but they are both complex and tedious^{12–15}.

At present, simple procedures based on the generation of volatile boron compounds and determination by atomic spectrometry are being developed because of the good sensitivity and selectivity obtained¹⁶.

Methyl borate has many advantages because of its simple generation conditions and its stability in the absence of moisture. New procedures for the generation of methyl borate without using external heating have also been investigated in order to produce a more rapid determination of boron^{17,18}.

In this study, a method involving flame AES in combination with FIA is described for the determination of B in a routine manner without any pre-concentration.

Experimental

Reagents and apparatus

All chemical products and solvents were of analytical grade (CARLO ERBA and MERCK). Deionized water was obtained via the MILLIPORE water system (Elix-10 followed by Milli-Q 185 Plus and 0.22 μm filter unit).

Boron stock solution: 2000 $\mu\text{g}/\text{mL}$, prepared by dissolving 5.72 g boric acid (MERCK) in 500 mL de-ionized water. This solution was kept in a polyethylene flask. Boric acid was first desiccated at 120°C to constant mass. Diluted solutions were freshly prepared before each analysis.

All experiments were carried out with an ATI-UNICAM 929 atomic absorption spectrometer, equipped with deuterium background correction.

For H₂SO₄ and CH₃OH flow injection system, a GILSON Minipuls 3 peristaltic pump was employed. Tygon tubings, green-green for methanol, blue-blue and blue-yellow for sulfuric acid were used, and all the other tubings used within the FIA were 0.8-1.0 mm (id) PTFE. Injections were performed via a 6-way valve.

The gas-liquid separator of a UNICAM VP90 Hydride Generation Unit was used. Ar was chosen as the carrier gas, and a 250 µL injection loop was used throughout the experiments.

Instrumental parameters

Emission measurements were carried out at 547.8 nm in the instrumental conditions that provide the best sensitivity. These conditions were 15mm of burner height with a 5cm burner head, at 1.0 nm spectral bandwidth, with 0.9 L/min C₂H₂ flow.

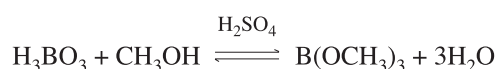
Proposed method

The method is based on the formation and volatilization of methyl borate. Castillo et al.¹⁸ had already optimized the reaction medium for the esterification as the methyl borate. The setup was changed accordingly to apply a FIA system and a gas-liquid separator was introduced to the system as well.

Atomic flame or non-flame techniques generally use a sample volume of 0.5-2 mL for the determination of a given element by continuous aspiration. Lower sample volumes can be assayed by using FIA in conjunction with such techniques. Unlike other detectors employed in FIA, atomic absorption spectrometers require no flow cell. The scheme for such a system is extremely simple; the carrier, pumped in a continuous fashion, is aspirated into the nebulizer.

An instrumental setup for boron determination by flow injection analysis (FIA) using methyl borate generation with a flame atomic emission spectrometer (FAES) as the detector was designed and is shown in Figure 1.

Methyl borate was generated according to the following reaction



Starting with the experimental values obtained by Castillo et al.¹⁸, such as 0.1 mL sample, 3 mL methanol and 1 mL sulfuric acid, the acid is supposed to be introduced to the system before the methanol and the generated gas is immediately sent to the nebulizer.

If volatilization of methyl borate is to occur, the volumes of sulfuric acid and methanol must be optimized and so the reaction conditions will be studied. This will be carried out by first varying the volume of methanol whilst keeping the volumes of sample and sulfuric acid constant. The influence of the aqueous volume of the boric acid sample on the formation of the methyl borate was studied next.

The gas-liquid separator (GLS) used to send the generated vapor into the nebulizer is shown in Figure 1 as well.

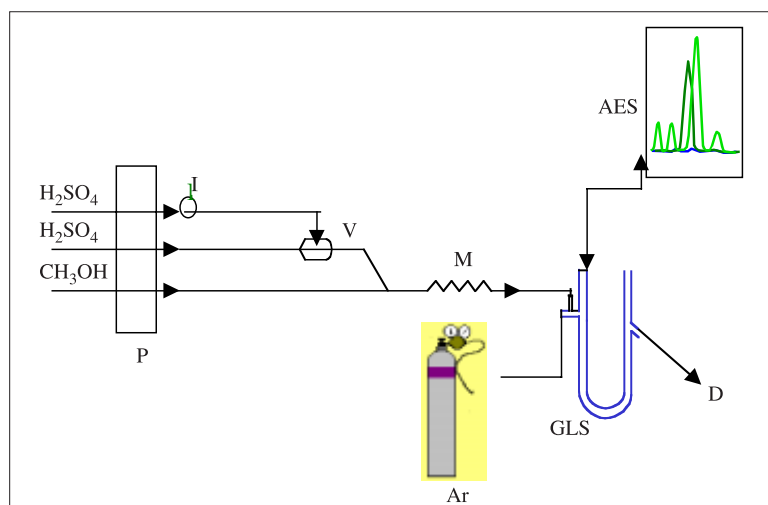


Figure 1. Schematic representation of the suggested experimental setup for **B** determination by the FIA-FAES technique. **P**, Peristaltic Pump; **I**, injection loop; **V**, 6-way valve; **M**, Mixing coil; **GLS**, Gas-Liquid Separator; **D**, Drain.

Results and Discussion

A fast and efficient method for the determination of boron in aqueous solutions is described using flame atomic emission spectrometry with flow injection analysis.

Sulfuric acid acts as a dehydrating agent that generates the heat necessary for the volatilization. The standard solutions were prepared in 60% (v/v) H_2SO_4 to obtain as much moisture-free medium as possible.

By using $200 \mu\text{g/mL}$ B in 60% (v/v) H_2SO_4 solution, the effect of Ar and pumping rates of reactants to the emission signal were observed and the results are given in Table 1. Accordingly, 30-rpm and 400 mL/min yield the best results. With those results the consecutive measurements were shown to be 1.6%RSD.

Table 1. The effect of carrier gas (Ar) and pumping rate of reactants on the signal.

Argon flow rate (mL / min)	Pump flow rate (rev / min)			
	15 rpm	20 rpm	30 rpm	35 rpm
300	16.2 ± 0.1	17.7 ± 0.6	22.6 ± 0.2	23.8 ± 0.4
400	15.5 ± 0.8	16.5 ± 0.2	23.7 ± 0.4	23.2 ± 0.7
500	14.8 ± 0.6	16.3 ± 0.2	22.0 ± 1.0	22.1 ± 0.7
600	14.1 ± 0.9	15.4 ± 0.8	20.6 ± 0.9	19.8 ± 1.3

Results are given as $X \pm S(n = 3)$.

Sulfuric acid 1, sulfuric acid 2 and methanol flow rates were measured for each pump rate (rev/min).

The effect of mixing coil length on the emission signal was studied next. The results are given in Table 2 and it is obvious that the length of the coil did not make any significant contribution to the sensitivity.

Table 2. The effect of mixing coil length on the emission signal. (100 mg/L B)

Length of mixing coil (cm)	10	30	53	70	164
Emission Signal	10.9 ± 0.4	10.5 ± 0.3	9.9 ± 0.1	10.3 ± 0.4	10.2 ± 0.8

Methyl borate formation should be carried out with a moisture-free medium. In order to fulfill this requirement, B solutions were prepared in various proportions of % H₂SO₄ (v/v) solutions and the results are given in Table 3.

Table 3. The effect of % H₂SO₄ on boron signal (25 µg/mL B).

% (v/v) H ₂ SO ₄	0	20	40	60
Emission Signal	1.95 ± 0.07	2.20 ± 0.30	2.95 ± 0.21	3.32 ± 0.18

According to the data, 60% (v/v) H₂SO₄ solution was used throughout the experiment.

In order to separate the gas portion of the generated methyl borate from its liquid parts, several gas-liquid separator designs were tested experimentally and the one shown in Figure 1 was chosen due to its highly efficient results.

The calibration graph shown in Figure 2 is linear between 10 and 2000 µg/mL and its equation is $y = 0.1105X - 1.496$; with Detection Limit (3 σ basis) 2.96 µg/mL or 0.74 µg B. A typical emission signal for boron takes 2-3 seconds to reach the peak summit and 45-60 seconds to return to the baseline.

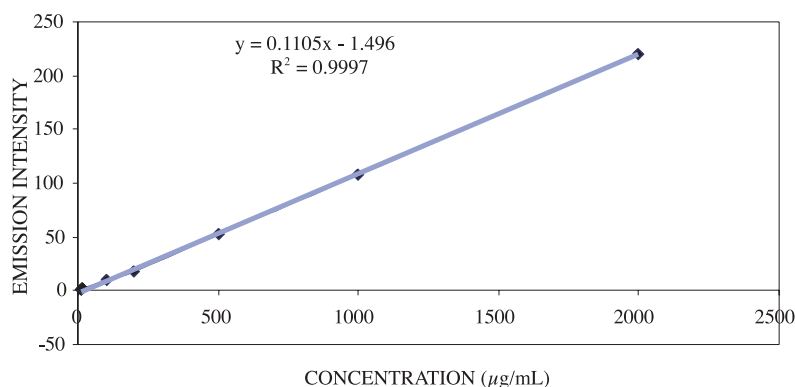


Figure 2. Calibration Graph for boron.

Due to its extremely poor sensitivity, it is difficult to determine B by AES and apparently a “standard method” is required.

To enhance the sensitivity and perform regular controls of B in different matrices without applying pre-concentration or extraction procedures, a reliable and convenient method has been proposed. The sensitivity of the method can be compared to other batch techniques, and therefore is recommended for routine laboratories.

It has been observed that the critical point of the method is the generation of methyl borate and its complete transfer to the nebulizer without any loss. Related parameters are the volume and design of GLS, suction rate of the nebulizer, mixing rate of solutions and the temperature of the reaction medium.

In our laboratory further studies will be carried out regarding the determination of B as organic and inorganic boron sources in soil.

Acknowledgment

We would like to thank *Prof. Dr. Tuncel ÖZDEN* for his never-ending encouragement and guidance throughout this study.

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