



Analytical Note

Alternative approaches to correct interferences in the determination of boron in shrimps by electrothermal atomic absorption spectrometry



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ABSTRACT

The aim of this study is to propose alternative techniques and methods in combination with the classical chemical modification to correct the major matrix interferences in the determination of boron in shrimps. The performance of an internal standard (Ge) for the determination of boron by the simultaneous multi-element atomic absorption spectrometry was tested. The use of internal standardization increased the recovery from 85.9% to 101% and allowed a simple correction of errors during sampling preparation and heating process. Furthermore, a new preparation procedure based on the use of citric acid during digestion and dilution steps improved the sensitivity of the method and decreased the limit of detection. Finally, a comparative study between the simultaneous multi-element atomic absorption spectrometry with a longitudinal Zeeman-effect background correction system, equipped with a transversely-heated graphite atomizer and the single element atomic absorption spectrometry with a D₂ background correction system, equipped with an end-heated graphite atomizer was undertaken to investigate the different behavior of boron in both techniques. Different chemical modifiers for the determination of boron were tested with both techniques. Ni-citric acid and Ca were the optimal chemical modifiers when simultaneous multi-element atomic absorption spectrometry and single-element atomic absorption spectrometry were used, respectively. By using the single-element atomic absorption spectrometry, the calculated characteristic mass was 220 pg and the calculated limit of detection was 370 µg/kg. On the contrary, with simultaneous multi-element atomic absorption spectrometry, the characteristic mass was 2200 pg and the limit of detection was 5.5 mg/kg.

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1. Introduction

Boric acid and its salts have antiseptic action and therefore are used as food preservatives. On the contrary, in two experiments on men it was found that doses of 1, 2, and 3 g of boric acid retarded the assimilation of albuminoids, the nitrogen contents of their urine being determined hourly before and after taking the boric acid [1,2]. Thus, a tolerable daily intake (TDI) for human consumption was established by World Health Organization (WHO), that is 0.16 mg B per kg body weight (bw) per day (d) [2]. There are several methods developed for the determination of boron [3–8]. Among them the most used are those which use the classical digestion analytical methods followed by atomic absorption spectrometry techniques [4,8] or inductively coupled plasma techniques for the determination of boron [5–7]. Inductively coupled plasma mass spectrometry (ICP-MS) is offering high sensitivity, low detection limits but is an expensive technique for one-element determinations [4,6,7,9]. Electrothermal atomic absorption spectrometry (ETAAS) could be used as an efficient technique for the determination of boron in foods due to the low cost and the low detection limits

compared to the levels of boron toxicity. ETAAS also suffers from a number of chemical interferences; the most common among them are: a) the formation of refractory boron carbides in the graphite tubes and b) the formation and the loss of boron oxides during the pyrolysis step or their incomplete dissociation during the atomization step. To solve these problems several methods have been proposed, such as the use of permanent chemical modifiers combined with Ni, Ca or organic acids in order to prevent the formation of boron carbides and oxides, respectively [4,8,10–12].

All studies for the determination of boron by ETAAS described the use of different potential chemical modifiers that managed to solve the problem of boron carbides and oxides. The current study has managed to propose alternatives techniques and methods to solve these two major problems in combination with chemical modification. Firstly, the performance of an internal standard for the determination of boron by Simultaneous Electrothermal Atomic Absorption Spectrometry (Simultaneous ETAAS) was tested. Germanium was chosen as an efficient internal standard. On the other hand, a new preparation procedure for the determination of boron in shrimp samples has been developed to avoid the loss of boron oxides during the digestion procedure. Finally, a comparative study of the simultaneous multi-element atomic absorption spectrometry (Perkin-Elmer SIMAA 6000) with a longitudinal Zeeman-effect background correction system, equipped

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with a transversely-heated graphite atomizer (THGA) and the classical electrothermal atomic absorption spectrometry (ETAAS, Perkin-Elmer 5000) with a D₂ background correction system, equipped with an end-heated graphite atomizer (HGA) was undertaken.

2. Experimental

2.1. Instrumentation

The measurements were carried out using a Perkin-Elmer SIMAA 6000 spectrometer equipped with a THGA graphite furnace with longitudinal Zeeman-effect background correction and an AS-72 autosampler and a Perkin-Elmer 5000 with a D₂ background correction system, equipped with a HGA 400 graphite furnace atomizer. A boron hollow cathode lamp and pyrolytically coated graphite tubes with or without L'vov platforms from Perkin-Elmer were used. For all measurements, integrated absorbance was recorded. The digestion procedure of shrimp samples was performed in a microwave oven, MARS X-Press (CEM Corporation, NC, USA).

2.2. Reagents

The following reagents were used throughout this work: HNO₃ 65% (v/v) *suprapur* grade (Merck, Germany); H₂O₂ 35% (v/v) *suprapur* grade (Merck, Darmstadt, Germany). A boron stock solution (1000 mg/L) was prepared by dissolving the appropriate amount of boric acid (Merck) in ultra-pure water (MilliQ water, Millipore, Bedford, MA, USA) and acidified to a final HNO₃ concentration of 1% (v/v). Working solutions of boron were made with appropriate dilutions with ultra-pure water. Boron isotopes were purchased from Sigma Aldrich (Taufkirchen, Germany). The chemical modifiers solutions were prepared from: zirconium oxychloride (ZrOCl₂·8H₂O 99%, BDH Chemicals, Arlington Heights, IL) dissolved in water; rhodium ammonium chloride ((NH₄)₃RhCl₆·H₂O 99.9%, Johnson & Matthey, London, United Kingdom) dissolved in 2.75 mol/L HCl; palladium 10 g/L (Merck) in HNO₃; platinum 1000 mg/L; nickel 1000 mg/L in 0.5 mol/L HNO₃; Co 1000 mg/L in 1% HNO₃ (Merck) and Cr 1000 mg/L in 1% (v/v) HNO₃ (Merck); ((NH₄)₂[Ru(H₂O)Cl₅] 1000 mg/L; nitrates of Ca, Mg in 1% (v/v) HNO₃ (High Purity Standards, Charleston, SC); calcium chloride 1000 mg/L; iridium 1000 mg/L, in 2% (v/v) HCl (High Purity Standards). Organic acids (citric acid, ascorbic acid) were prepared with appropriate dilutions with ultra-pure water. Germanium 1000 mg/L (High Purity Standards) was used as an internal standard. Due to the fact that boron is contaminated in glass all the containers for this study were made of plastic, and were rinsed with 1% (v/v) nitric acid.

2.3. Procedure

When simultaneous ETAAS was used, the following protocol for the digestion of shrimp samples was followed: 0.5 g of homogenized shrimp samples were weighted into the Teflon vessels and 5 mL of concentrated HNO₃ was added. The samples were digested with the MARS X-Press (CEM Corporation, NC, USA) microwave oven in a pre-selected program (first stage at 1600 W and 165° C for 2 min; second stage at 1600 W and 175° C for 8 min) and then diluted in a final volume of 20 mL with ultrapure water. When Ge was used for internal standardization, the same protocol was followed after the addition of 100 µg Ge/L into the Teflon vessels.

When classical ETAAS was performed, seven different preparation procedures were examined based on the classical digestion methods and the addition of citric acid during the digestion and the dilution steps. The following protocols were examined:

a) 0.5 g of the shrimp samples were weighted into the Teflon vessels and 5 mL of 65% HNO₃ and 1 mL H₂O₂ (30%) were added. The samples were digested in the MARS X-Press (CEM Corporation, NC, USA)

following the same pre-selected programme and then diluted in a final volume of 20 mL with ultrapure water.

- As protocol (a), but the final dilution was made in 20 mL of citric acid (20 g/L) to test if the addition of citric acid during the dilution step improves the sensitivity.
- As protocol (b), but no H₂O₂ was added for testing if the addition of citric acid in combination with the absence of H₂O₂ during the digestion and the dilution steps improves the sensitivity.
- As protocol (b), but 2 mL of citric acid (20 g/L) were added along with HNO₃ and H₂O₂ for testing if the addition of citric acid during the digestion and the dilution step improves the sensitivity in the presence of H₂O₂.
- As protocol (d), but the dilution was made in ultra-pure water for testing if the addition of citric acid during the dilution step is necessary for improving the sensitivity.
- As protocol (d), but no H₂O₂ was added in order to investigate if the addition of citric acid during the digestion and the dilution steps is necessary for improving the sensitivity in the absence of H₂O₂.
- As protocol (f), but the final dilution was made in ultra-pure water for testing if the addition of citric acid during the dilution steps is not necessary for improving the sensitivity in absence of H₂O₂.

3. Results and discussion

3.1. The simultaneous multi-element electrothermal atomic absorption spectrometry approach

The simultaneous ETAAS approach was used because the internal standardization quantification technique can be used. Ge was chosen as an internal standard because its physicochemical properties may resemble those of boron (it forms volatile and very stable oxides). A comparative study of various potential chemical modifiers (Ca, Cr, Co, Ir, Mg, Ni, Pd, Pt, Rh, Ru, Sr, Ta, Ti, Zr, Zr + Ir, Zr + Ni, Cr + citric acid, Ni + ascorbic acid, Ni + citric acid, Zr + citric acid, Ni + Zr + citric acid) for the determination of boron was undertaken. Among the chemical modifiers tested Ca, Co, Ir, Mg, Pd, Pt, Rh, Ru, Sr, Ta, Ti, Zr + Ir showed poor performance. Refractory carbide forming elements such as Zr permitted using a pyrolysis temperature up to 1600° C without significant analyte losses. The performance of Cr improved the sensitivity of boron determination but it provided a less thermal stabilization compared with Zr ($T_{\text{pyr}} = 1000$ °C). Cr forms metal borides, such as CrB₂, CrB, Cr₅B₃ and Cr₂B that are produced by the reaction of B₄C with Cr [13]. Nickel, that also forms metal borides, seems to be less effective than Cr and Zr ($m_o = 5.1$ ng, $m_o = 2.9$ ng and $m_o = 3.8$ ng, respectively) with respect to sensitivity.

The combination of Ni or Cr with an organic acid, especially citric acid, provided the best performance improving the characteristic mass and decreasing the limit of detection, due to the production of active carbon leading to the reduction of boron oxides [14].

In this study, the combination of 5 µg Cr with 100 µg citric acid ($m_o = 1$ ng) was proved to be the most efficient chemical modifier, followed by the combination of 1.25 µg Ni with 100 µg citric acid ($m_o = 1.3$ ng). However, when the combination of 50 µg Zr with 100 µg citric acid was tested, the sensitivity was decreased ($m_o = 5.2$ ng) compared to the sensitivity achieved when 50 µg Zr was added as chemical modifier ($m_o = 3.8$ ng). This may be caused due to the reaction of Zr with carbon of citric acid which decreases the activity of both modifiers. This fact is also proved by the decrease of sensitivity when 50 µg Zr were added along with 100 µg citric acid and 1.25 µg Ni ($m_o = 1.8$ ng) compared to the combination of 1.25 µg Ni with 100 µg citric acid ($m_o = 1.3$ ng). The combinations of Cr, Zr and Ni with ascorbic acid were also tested. Ascorbic acid was proved to be less effective than citric acid (e.g. when 40 µg ascorbic acid were combined with 1.25 µg Ni the sensitivity was decreased from 1.3 ng to 2.0 ng compared to the combination of 1.25 µg Ni with 100 µg citric acid). In general, the use of an organic acid improved the sensitivity of

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