



## Evaluation of lines of boron, phosphorus and sulfur by high-resolution continuum source flame atomic absorption spectrometry for plant analysis

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### ABSTRACT

The wavelength-integrated absorbance (WIA) and summation of absorbance ( $\Sigma$  lines) of different lines were evaluated to enhance sensitivity and determine B, P and S in medicinal plants by HR-CS FAAS. The lowest LOD for B ( $0.5 \text{ mg L}^{-1}$ ) and P ( $13.7 \text{ mg L}^{-1}$ ) was obtained by integration of lines 249.773 nm (3 pixels) and 247.620 nm (5 pixels), respectively. The  $\Sigma$  lines for CS at 257.595 nm and 257.958 nm furnished LOD =  $30.5 \text{ mg L}^{-1}$ , ca. 10% lower than the LOD obtained for the WIA using 257.595 nm and 5 pixels. Data showed the advantage of WIA over  $\Sigma$  lines to improve sensitivity for all analytes. Under optimized conditions, calibration curves in the 1.0–100  $\text{mg L}^{-1}$  B and 50.0–2000  $\text{mg L}^{-1}$  P, S ranges were consistently obtained. Results obtained with the HR-CS FAAS method were in agreement at 98% and 95% confidence level with certified values for B and P, respectively. And results for S were in accordance to non-certified values. Concentrations of B, P, and S in 12 medicinal plants analyzed by the proposed method varied within the 19.4–34.5  $\text{mg kg}^{-1}$  B, 719–3910  $\text{mg kg}^{-1}$  P and 1469–7653  $\text{mg kg}^{-1}$  S ranges.

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### 1. Introduction

Foliar diagnosis is an efficient tool in agriculture to manage the mineral nutrition of plants [1]. The monitoring of nutrients in crop leaves allows the identification of deficiency, sufficiency or excess of a given element, optimization of crop production and evaluation of fertilizer supplies [2]. Boron, phosphorus and sulfur are among the main nutrients usually required in foliar diagnosis.

Spectrophotometry and inductively coupled plasma optical emission spectrometry are the customary analytical techniques employed in large-scale routine analysis of plants for B [3], P [4], and S [5].

Among the spectrometric techniques available for the determination of most macro- and micronutrients in plants, the line source flame atomic absorption spectrometry (LS-FAAS) is the oldest and most commonly used [6]. However, the difficulty of measuring absorbance of P within the 167.167 nm–178.765 nm, S within the 180.671 nm–182.565 nm spectral ranges, and the poor sensitivity of non-resonance lines of P at 213.618 nm, 213.547 nm, and 214.914 nm, may be considered as the main drawbacks to the determination of phosphorus [7] and sulfur [8] by LS-FAAS. But these drawbacks can be circumvented measuring at molecular lines of PO and CS by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) [9–12]. The low sensitivity of B determination by LS-FAAS (results of the small atomization degrees of B in flames) may be improved using the high

intensity xenon short-arc lamp of the HR-CS FAAS. The sequential multi-element analyses, the summation of absorbance signals [13] of main and secondary atomic lines resulting in a new calibration function and the integration of the absorbance signal over the center pixel by including part of the line wings [14] are facilities of the HR-CS FAAS to improve the sensitivity. For routine laboratories devoted to large-scale analyses, fast sequential multi-element determination is particularly helpful because time and analytical costs may be significantly reduced.

Little attention has been given to the use of the summation of absorbance and integration of the absorbance to increase sensitivity in the sequential multi-element determination of B, P and S in plants by HR-CS FAAS.

This paper reports an evaluation and application of the HR-CS FAAS technique in the determination of B, P and S for plant analysis. The influence of the nature of line (atomic or molecular), the summation of absorbance at these lines and the variation of number of pixels on sensitivity, accuracy and precision were studied.

### 2. Materials and methods

#### 2.1. Instrumentation

A contrAA 300 (Analytik Jena, Germany) high-resolution atomic absorption spectrometer equipped with a xenon short-arc lamp operating in the “hot-spot” mode as a continuum radiation source was used throughout the work. Air-acetylene flame was used for PO and CS production, and a fuel-rich nitrous oxide-acetylene flame was used for B atomization. High-purity acetylene (99.7% Air Liquid, SP,

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Brazil) and high purity nitrous oxide (99.5% Air Liquid) were used as fuel gas and oxidant gas, respectively. All measurements were carried out in seven replicates at aspiration rate fixed at  $5.0 \text{ mL min}^{-1}$ . The optimum nitrous oxide–acetylene flow rates were  $462$  and  $245 \text{ L h}^{-1}$  (B). And the optimum air–acetylene flow rates were  $594$  and  $100 \text{ L h}^{-1}$  (PO),  $594$  and  $120 \text{ L h}^{-1}$  (CS).

## 2.2. Reagents and analytical solutions

High purity de-ionized water obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q™ Academic® deionizer system (resistivity  $18.2 \text{ M}\Omega \text{ cm}$ , Millipore, Bedford, MA, USA) was used throughout to prepare all solutions.

A  $5000 \text{ mg L}^{-1}$  P standard stock solution was prepared by dissolving  $34.874 \text{ g Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$  (Riedel-De Hën, Seelze, Germany) in water and making the volume up to  $1000 \text{ mL}$  with water.

A  $5000 \text{ mg L}^{-1}$  S standard stock solution was prepared by dissolving  $38.434 \text{ g MgSO}_4 \cdot 7\text{H}_2\text{O}$  (Spectrum, Gardena, CA, USA) in water and making the volume up to  $1000 \text{ mL}$  with water. This salt was standardized against gravimetry by making a precipitate of barium sulfate and weighing the isolated pure compound.

A  $1000 \text{ mg L}^{-1}$  B stock standard solution was prepared by dissolving  $5.719 \text{ g H}_3\text{BO}_3$  (Spectrum, Gardena, CA, USA) in water, and making the volume up to  $1000 \text{ mL}$  with water.

A  $5000 \text{ mg L}^{-1}$  Ti stock standard solution was prepared by diluting the Titrisol® standard (Merck, Germany) in  $200 \text{ mL}$  water.

Multi-element analytical solutions ( $1.0$ – $100.0 \text{ mg L}^{-1}$  B,  $50.0$ – $2000 \text{ mg L}^{-1}$  P and  $50.0$ – $2000 \text{ mg L}^{-1}$  S) were daily prepared by proper dilution of single stock standard solutions. All solutions were stored in high-density polypropylene bottles (Nalgene®, Rochester, NY, USA). Plastic bottles and glassware materials were cleaned by soaking in  $10\%$  (v/v)  $\text{HNO}_3$  at least  $24 \text{ h}$  and rinsed abundantly in deionized water before use.

## 2.3. Sample preparation

Medicinal plants of *Peumus boldus*, *Matricaria chamomilla*, *Baccharis trimera*, *Echinodorus grandiflorus*, *Pimpinella anisun*, *Maytenus ilicifolia*, *Ginkgo biloba*, *Panax ginseng*, *Annona muricata*, *Mentha* spp., *Mentha pulegium* and *Cassia angustifolia* were purchased at local market in Araraquara city, SP, Brazil.

The certified standard reference materials Trace Elements in Spinach Leaves (1570a) and Apple Leaves (1515) (National Institute of Standards and Technology, Gaithersburg, MD) and samples were mineralized in triplicate using nitric acid and hydrogen peroxide. To  $2000 \text{ g}$  of dried powdered materials placed into  $400\text{-mL}$  digestion tubes,  $3.5 \text{ mL}$  of  $30\%$  (v/v)  $\text{H}_2\text{O}_2$  (Spectrum, Gardena, CA, USA) was added and let the mixture stand overnight. Thereafter,  $10 \text{ mL HNO}_3$  (Spectrum, Gardena, CA, USA) was added and the tubes were placed on a block digester at  $90 \text{ }^\circ\text{C}$  for  $2 \text{ h}$ . The temperature was increased to  $150 \text{ }^\circ\text{C}$  and the solution was evaporated to near dryness. The residue was then taken up in water, filtered, added  $5 \text{ mL}$  of  $5000 \text{ mg L}^{-1}$  Ti, and the volume was completed to  $25 \text{ mL}$  with water.

## 2.4. Analytical procedure

Measurements were carried out at the main and secondary atomic lines for B ( $249.773 \text{ nm}$  and  $249.677 \text{ nm}$ ), at PO molecular lines for P ( $246.400$ ;  $247.620$  and  $247.780 \text{ nm}$ ) and CS molecular lines for S ( $257.595$ ;  $257.958 \text{ nm}$ ).

In HR-CS AAS it is possible to apply the wavelength-integrated absorbance (WIA) over the line core including part of the line wings to enhance sensitivity. The influence of WIA on the linear dynamic range (LDR), sensitivity, linear correlation coefficient (R), characteristic concentration ( $C_0$ ), limit of detection (LOD), limit of quantification (LOQ) and precision was evaluated by varying different number of

pixels used for detection: 1 pixel (central pixel, CP), 3 pixels ( $\text{CP} \pm 1$ ), 5 pixels ( $\text{CP} \pm 2$ ), and 7 pixels ( $\text{CP} \pm 3$ ). The integrated area has little differences in width due to the resolution of the equipment; each wavelength has a bandwidth per pixel. Table 1 shows spectrometric data to all elements determined. The WIA was applied to individual and summed lines of all analytes.

For  $5 \text{ mL min}^{-1}$  sampling rate, analytical curves in the  $1.0$ – $100 \text{ mg L}^{-1}$  B,  $50.0$ – $2000 \text{ mg L}^{-1}$  P and  $50.0$ – $2000 \text{ mg L}^{-1}$  S concentration ranges were consistently obtained using the lines  $249.773 \text{ nm}$ ,  $247.620 \text{ nm}$ , and  $257.595 \text{ nm}$ , and integration equivalent to 3, 5 and 5 pixels, respectively.

The limit of detection (LOD) and limit of quantification (LOQ) for all analytes were calculated according to the IUPAC recommendation [15].

## 3. Results and discussion

The high signal-to-noise ratio of the continuum radiation source, the accessibility to alternate lines for PO and CS molecules, and the possibility to enhance sensitivity with the WIA [14] and summation of absorbance of different lines [13] are favorable attributes to investigate the feasibility of fast sequential multi-element determination of B, P, and S in a single aliquot of plant digests by HR-CS FAAS. The instrumental operating conditions were then maximized employing the most sensitive lines for B (doublet at  $249.773$  and  $249.677 \text{ nm}$ ), PO ( $246.400$ ,  $247.620$  and  $247.780 \text{ nm}$ ) and CS ( $257.595$  and  $257.958 \text{ nm}$ ) [7–9]. The sample preparation procedures were adapted to higher masses of herbal plants taking into consideration the low contents of B, P and S usually found in these plant tissues.

The main figures of merit (slope and linear correlation coefficient of the calibration curve, characteristic concentration, limit of detection and relative standard deviation) related to individual lines and summation of lines ( $\Sigma$  lines) at different number of pixels for detection (CP,  $\text{CP} \pm 1$ ,  $\text{CP} \pm 2$ ,  $\text{CP} \pm 3$ ) are described in Tables 2, 3 and 4 for B, P and S, respectively.

Analysis of Table 2 reveals that analytical curves built up in the  $1.00$ – $100 \text{ mg L}^{-1}$  B ranges for  $249.773 \text{ nm}$ , and  $2.00$ – $100 \text{ mg L}^{-1}$  to  $249.677 \text{ nm}$  and  $\Sigma$  lines presented linear correlation coefficients better than  $0.998$ . When the number of pixels was ranged from 1 to 7, slopes of analytical curves for  $249.773 \text{ nm}$ ,  $249.677 \text{ nm}$  and  $\Sigma$  lines increased from  $1.872 \cdot 10^{-4}$  to  $8.693 \cdot 10^{-4}$ ,  $9.661 \cdot 10^{-5}$  to  $4.387 \cdot 10^{-4}$ , and  $2.839 \cdot 10^{-4}$  to  $1.310 \cdot 10^{-3}$ , respectively. And the characteristic concentrations ( $C_0$ ) reduced from  $23.5$  to  $5.1 \text{ mg L}^{-1}$  ( $249.773 \text{ nm}$ ),  $45.5$  to  $10.0 \text{ mg L}^{-1}$  ( $249.677 \text{ nm}$ ), and  $15.5$  to  $3.3 \text{ mg L}^{-1}$  ( $\Sigma$  lines).

For any number of pixels used for detection, the lowest LOD was obtained for the main line at  $249.773 \text{ nm}$ , followed by the  $\Sigma$  lines and  $249.677 \text{ nm}$ . The summation of lines did not contribute significantly to improve the LOD due to the different sensitivity of B atomic lines. In this situation, noise was the major contribution of the secondary line to the main line at  $249.773 \text{ nm}$ . However the main use of lines with different sensitivities is the expansion of the linear range [16].

The main line at  $249.773 \text{ nm}$  and WIA equivalent to 3 pixels ( $\text{CP} \pm 1$ ) was selected for B determination in further works taking into

**Table 1**  
Spectrometric data for the determined elements.

Element	Wavelength (nm)	Bandwidth per pixel/pm
B	249.773	1.45
	249.677	1.45
P (PO)	246.400	1.29
	247.620	1.40
	247.780	1.40
S (CS)	257.595	1.42
	257.958	1.42

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