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The determination of boron in tea and coffee by ICP–AES method

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Abstract

A method for determination of boron by optical emission spectrometry with inductively coupled plasma has been suggested and sufficient experimental conditions have been found. The effect of the presence of Na, K, Mg, Ca, HCl, HNO_3 on the determination of boron has been studied. The internal standardisation as a correction technique was explored (In). The accuracy of the method was validated using the Chinese reference material GBW 07605 Tea. The efficiency of microwave digestion technique and hot water extraction was studied. The method was applied to the analyses of hot water extracts of tea and coffee samples. The mean extracted amount of boron ranged from 3.21 ± 0.17 to 9.25 ± 0.421 mg kg^{-1} in black teas; 3.54 ± 0.12 to 5.52 ± 0.15 mg kg^{-1} in green teas; 2.71 ± 0.13 to 27.7 ± 0.9 mg kg^{-1} in fruit teas; 13.3 ± 0.4 to 21.3 ± 0.7 mg kg^{-1} in instant coffees and from 7.57 ± 0.26 to 17.5 ± 0.5 mg kg^{-1} in ground roasted coffee beans.

Keywords: Boron; ICP–AES; Matrix influence; Internal standardisation; Microwave digestion; Hot water extraction

1. Introduction

Boron is a beneficial element for humans and animals (Nielsen, 1993), but its requirement for human has not been proved yet, and its meaning is undervalued. Boron is an essential element. Due to the fact that organism needs boron only in small amounts the minimum daily dose has not been determined. Boron stimulates brain function and together with other minerals, such as calcium and magnesium and vitamin D it helps to prevent osteoporosis. It is contained in fresh fruit and vegetables, mainly in plums and apricots. As a nutrient complement 3 mg boron per day is recommended (Mindell, 2000; Nielsen, 1993). Boron is an indispensable element for plants and its deficiency affects plant growth and yield and limits crop productivity. However, substantial amounts of boron are toxic to plants and reduce plant yields (Novozámský, Houba, Vanderlee, Vaneck, & Mignorance, 1993).

The analytical techniques used for determination of boron range from simple electrochemical methods to complex nuclear methods (Sah & Brown, 1997). Most of the methods originally used were based on spectrophotometric and fluorimetric determination of coloured or fluorescent products of reactions with organic dyes (azomethine-H, curcumin, quinalizarine, arzenazo, methylene blue and crystal violet for spectrophotometry, Alizarin Red S and chromotropic acid for fluorimetry). The fluorimetric methods are more sensitive than the photometric methods, but are more susceptible of interference by a number of chemical species and are sensitive to pH and temperature. Therefore, fluorimetric methods are not as widely used as colorimetric methods (Anárez & Mir, 1984; Sah & Brown, 1997; Wimmer & Goldbach, 1999).

Potentiometric methods usually need separation of boron from the sample matrix. They have not been very popular and widespread (Sah & Brown, 1997). Flame technique, for example, flame atomic absorption spectrometry and flame atomic emission spectrometry, generally have unsatisfying detection limits for boron and mostly require separation of boron from the sample matrix. The atomic absorption spectrometry with

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electrothermal vaporisation allows determination of boron in liquid or solid samples without sample digestion but without application of chemical modifiers or modification of tube surface it has poor detection limits. Other preparation procedures leading to required sensitivity and precision of method are both time and money consuming therefore, they have not been extensively used (Sah & Brown, 1997; Szydlowski, 1979).

Both ICP–OES and ICP–MS provides a fast multielemental analysis. Their advantage over other methods lies in higher sensitivity, lower detection limits and simultaneous measurement of elements. The ability of ICP–MS to determine boron isotope ratios makes it suitable for biological studies. The multielement determination of major-to-ultratrace elements in plant reference materials (SRM Pine Needles, SRM Tomato Leaves, and NIES Tea Leaves) was carried out by ICP–AES and ICP–MS after decomposition with nitric acid and hydrofluoric acid (Hokura, Matsuura, Katsuki, & Haraguchi, 2000).

Simpkins, Louise, Wu, Harrison, and Goldberg (2000) determined the concentrations of 22 trace elements including B in 482 samples of Australian and Brazilian orange juices and Australian peel extracts and deacidified juices using ICP–AES/MS.

The ICP–AES method was used for determination of boron plant samples (Kovács, Györi, Prokisch, Loch, & Dániel, 1996), in liquid nutritional food (Szabó & Golightly, 1995), in Hungarian red wines (Szentmihályi et al., 2000), in dried onion, leaves of spinach beet, reference materials (Borkowska-Burnecka, 2000).

2. Material and methods

2.1. Reagents and materials

Black, green and fruit tea sorts, ground roasted bean coffees and instant coffees available in the Czech Republic were analysed. The accuracy of the study was validated using the Chinese reference material GBW 07605 Tea.

The single component standards of B, In and Cu (each one with the content of 1.000±0.002 mg g^{-1}, Analytika, Czech Republic) were used. For the matrix effect study, analytical grade concentrated (65%) HNO_3 and (35%) HCl (Lachema, Czech Republic) were used. NaCl, KCl, $CaCl_2$, $MgCl_2$ were of “purity pro analyse” grade, from Lachema (Brno, Czech Republic). The demineralised water was taken from a Milli-Q Plus water-purification system (Millipore, Bedford, USA).

The set of calibration standards contained 0.005, 0.01, 0.05, 0.1, 0.5, 1.0, 5.0, 10.0 mg l^{-1} of boron. The whole set was used for the matrix interference study and evaluation of calibrations. In the case of analysis of real samples, only three standards were used (0.1, 1.0 and 5.0 mg l^{-1}). Internal standards Cu and In were used in the matrix interference study (1 mg l^{-1} of copper or 10 mg l^{-1} of indium). The set of calibration standards used for analysis of microwave digests contained added amount of HNO_3 (28 ml 65% HNO_3 in 100 ml solution) and internal standard indium.

2.2. Sample treatment

Prior to analysis, samples were homogenised and prepared for ICP analysis using two procedures: total decomposition and a hot water extraction (Webb, Hanks, & Jolley, 2002). The total decomposition was carried out in a microwave digestion unit Plazmatronika, model BM-1S/II (Plazmatronika, Poznan, Poland). About 0.3–0.4 g of tea or coffee were accurately weighed into an acid washed teflon digestion tube. Seven millilitres of concentrated nitric acid [65% (m/v)] was added, and the tube was heated in a microwave oven at the power setting of 80% for 10 min and at 100% for 10 min. The maximum total output of the microwave generator was 700 W (minimum pressure = 24.32 10^5 Pa, maximum pressure = 25.33 10^5 Pa). The digest was transferred into a 25 ml acid washed volumetric flask, filled up with demineralised water and stored in polypropylene flasks. Two water blanks were run with each batch of samples. The hot water extraction: about 1.0 g of tea or coffee was accurately weighed into an acid washed beaker and extracted with 50 ml boiling demineralised water. After 5 min the extract was filtered into a 100-ml acid washed volumetric flask, 1 ml concentrated nitric acid was added (for stabilising the solution), filled up with demineralised water and stored in a polyethylene flask.

2.3. Analytical method

The measurements were carried out with an ICP atomic emission spectrometer “Integra XL 2” from GBC Australia. The used emission lines of boron were B I 249.773 nm, B I 249.678 nm, and B I 208.959 nm. The line of internal standard indium (In I 325.609 nm) and cooper (Cu I 324.754 nm) were used for matrix effect correction. The operating condition was as followed: plasma power supply 1.0 kW, observation height 6 mm, plasma gas flow 10.0 l min^{-1}, auxiliary gas flow 0.5 l min^{-1}, nebuliser gas flow 0.6 l min^{-1}, photomultiplier voltage 600 V, sample uptake rate 1.7 ml l^{-1}, integration time 1 s, sample time delay 30 s.

2.4. Quality control and statistical methods

Running repetitive microwave digestion and hot water extraction of reference material GBW 07605 Tea tested the precision and efficiency of method. A number of analytical quality control procedures were adopted to reduce uncertainty. Internal standards were used to compensate for possible matrix interference variations in case of analysis of microwave digests. External standards used for calibration were regularly reinjected after every ten samples to reveal a potential shift of initial calibration. The samples were also spiked with boron at above 50% of their natural concentration. The uncertainty of estimates was based on repeated analyses of samples and reference material.

Statistical calculations were realised with the use of the statistical PC program ADSTAT 2.0 (Trilobyte Statistical Software, Pardubice, Czech Republic). The calibration dependences for all three boron lines were evaluated:

$$I_{\mathrm{B\ I}\ 249.773} = 939.1(328.9) + 253540(878.0)c_{\mathrm{B}}\ (R^2 = 0.9999)$$

$$I_{\mathrm{B\ I}\ 249.678} = 3368(1304) + 129520(348.3)c_{\mathrm{B}}\ (R^2 = 0.9995)$$

$$I_{\mathrm{B\ I}\ 208.959} = 1003(195.5) + 6266(52.20)c_{\mathrm{B}}\ (R^2 = 0.9986),$$

where I_{B} [count] is intensity of boron line, c_{B} [mg l^{-1}] is concentration of boron, and R^2 is the coefficient of determination. The test of linearity proved that the dependences were linear (the test of quadratic term significance).

The limit of determination x_{s} (Meloun & Militky, 1994) and 3σ (IUPAC convention) were determined (in mg l^{-1}):

$$x_{\mathrm{s\ B\ I}\ 249.773} = 0.0067,$$

$$x_{\mathrm{s\ B\ I}\ 249.678} = 0.0087,$$

$$x_{\mathrm{s\ B\ I}\ 208.959} = 0.0206,$$

$$3\sigma_{\mathrm{B\ I}\ 249.773} = 0.0031,$$

$$3\sigma_{\mathrm{B\ I}\ 249.678} = 0.0040,$$

$$3\sigma_{\mathrm{B\ I}\ 208.959} = 0.0122.$$

3. Results and discussion

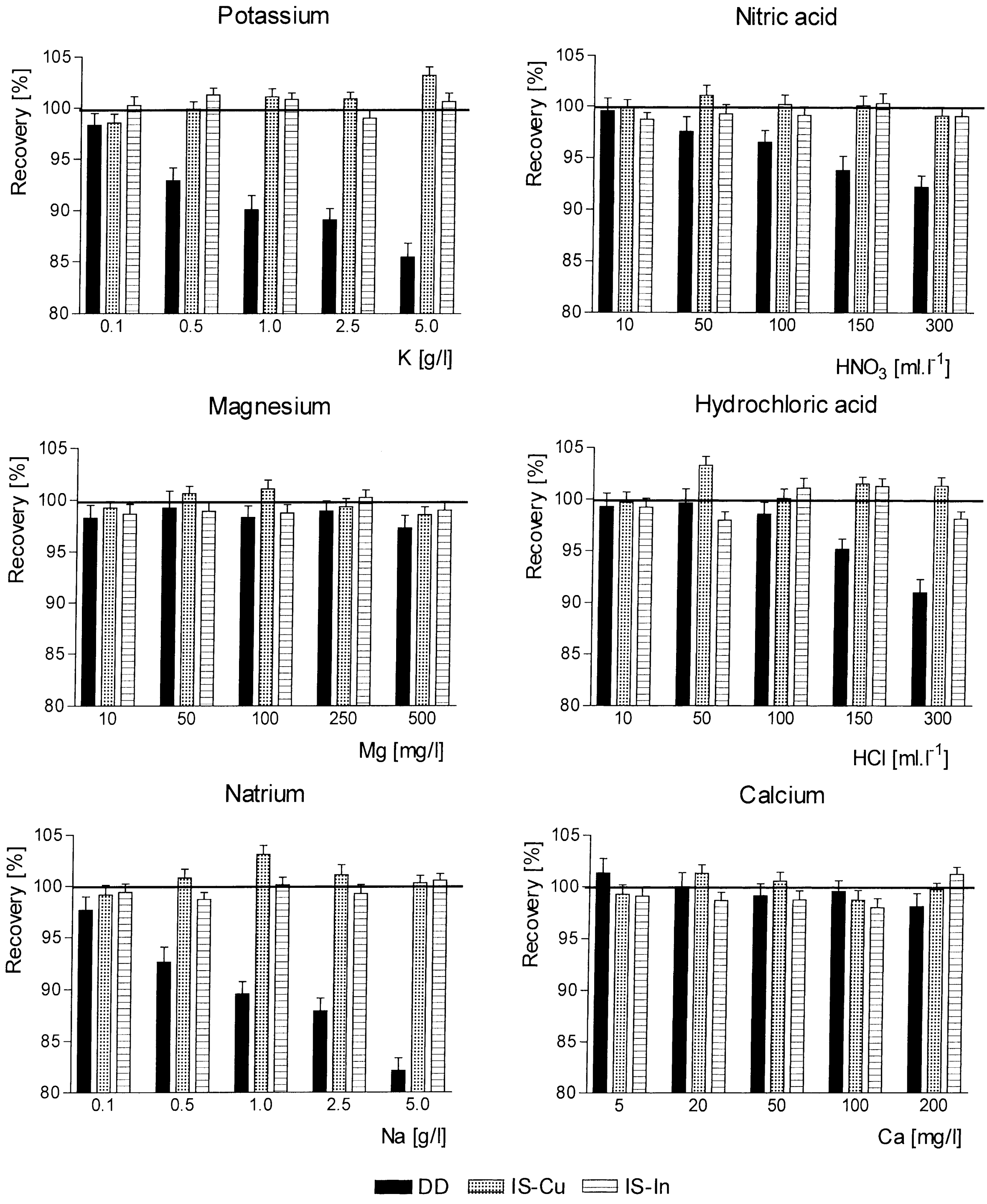
3.1. Study of matrix interferences in model samples

Potential matrix interfering species (HNO_3, HCl, Na, K, Mg and Ca) were tested. Nitric and hydrochloric acids are commonly used decomposition agents, Na, K, Mg, and Ca is plant matrix elements. The matrix components influence (Na, K, Ca, Mg, Hcl, HNO_3) and their concentration levels were studied on spectral lines B I 249.773 nm, B I 249.678 nm, B I 208.959 nm (graph 1a–f). The concentration levels of Na and K ranged from 100 to 5000 mg l^{-1}. The intensity of boron signal decreased in case of all three spectral lines by up to 15%. The concentration of Ca ranged from 5 to 200 mg l^{-1} and Mg ranged from 10 to 500 mg l^{-1}. No significant signal decrease was observed in case of Mg and Ca. The tested mineral acids also depressed the boron intensity. The signal decrease of up to 7% was observed in both cases. Results of matrix effect study were statistically estimated. The analysis of variance approved marginal concentrations of tested matrix components that significantly influenced boron signal intensity: Na, K and Mg from 0.5 g l^{-1}, Ca from 0.2 g l^{-1}, HCl and HNO_3 from 10 ml of concentrated acid in 100 ml solution.

A proper choice of an internal standard makes the transport interference and, particularly, ionisation interference to decrease. The internal standards used in matrix interference study were copper and indium. The earlier-mentioned boron solutions with tested matrix components were evaluated by internal standardisation method. Recoveries of this determination are displayed in graphs 1a–f. The results of boron determination with copper and indium used as the internal standards were very similar. Both the internal standards successfully eliminated the acid effect. Both elements can be used for this purpose. The influence of Na and K was not eliminated completely but the internal standardisation improved the determination recoveries. According to literature data (Krejčová, Černohorský, & Čurdová, 2001; Masson, 1999), the resultant matrix effect of a set of components is lower than the sum of the single matrix component additions. A combined influence of acids and the other elements was not tested.

3.2. Digestion and Extraction

The determination of iron, copper, sodium, potassium, magnesium and calcium in microwave digests (MD) and hot water extracts (HWE) was carried out. Iron interferes with the two most sensitive B lines 249.773 nm and 249.678 nm. The influence of Fe on boron line 249.678 nm was tested. The concentration of 0.5 g l^{-1} Fe measured in the mentioned boron line did not produce any detectable boron concentration readout. A higher iron concentration in digests and extracts was not supposed. The concentration of iron in chosen hot water extracts ranged from 0.01 to 0.1 mg l^{-1}. The presence of copper in tea and coffee samples makes it impossible to adopt Cu as the internal standard (concentration of copper in extract was about 0.02 mg l^{-1}); therefore, indium was used instead. The other elements (Na, K, Mg and Ca) were analysed in order to assess their potential matrix effect. Because of the concentration of Na, K, Mg and Ca in hot water extracts was relatively low (Na 0.01–0.02, K 0.1–100, Mg 0.5–100 and Ca 1–100 mg l^{-1}), matrix interference due to their



Graph 1. (a–f) Effect of tested matrix components (line B I 249.678 nm)—the direct determination (DD), the internal standard Cu (IS-Cu), the internal standard In (IS-In).

presence was not supposed, the internal standardisation was not necessary and only a direct determination of boron in hot water extracts was carried out. The mean values of boron for repeated microwave digestions and hot water extraction of the Chinese reference material GBW 07605 Tea and chosen tea and coffee samples are shown in Table 1. Each sample was digested and extracted six times. Each extract was measured five times. Results of boron content are the average values determined from spectral line B I 249.773 nm and B I 249.678 nm. The chosen samples were also spiked with boron at above 30–80% of their natural concentration. These adjusted samples were used for control of correctness of microwave digestion.

Table 1
Analysis of GBW 07605 Tea and tea and coffee samples

	MD–DD	MD–IS	HWE–DD	HWE/MD [%]
		[mg kg^{-1}]		
GBW 07605 (15±3 mg kg^{-1} B)	14.3±0.8	15.3±0.6	6.75±0.22	41.8
GBW 07605, spiked 5 mg kg^{-1} B	19.2±1.1	19.7±0.6		
Black tea[a]	13.6±0.8		5.40±0.18	39.8
Black tea[a], spiked 5 mg kg^{-1} B	19.0±1.0			
Fruit tea[b]	18.6±1.6		6.05±0.45	32.6
Fruit tea[b], spiked 5 mg kg^{-1} B	23.0±2.3			
Coffee beans[c]	6.66±0.34		3.28±0.16	49.2
Coffee beans[c], spiked 5 mg kg^{-1} B	11.3±0.7			
Instant coffee[d]	13.0±0.7		11.8±0.67	90.6
Instant coffee[d], spiked 5 mg kg^{-1} B	18.6±1.2			

MD–DD microwave digestion and direct determination of boron; MD–IS microwave digestion and internal standardisation; and HWE–DD hot water extraction and direct determination of boron.

[a] Pigi tea (Jemča, a.s., Czech Republic).

[b] Garden fruit (Leros s.r.o., Czech Republic).

[c] Douwe Egerts, mix (Balírny Douwe Egberts, a.s., Czech Republic).

[d] Nescafé Classic (Nestlé Food s.r.o., Czech Republic).

Table 2
The minimum and maximum amounts of boron in tea and coffee samples

	Number of samples	Minimal amount [mg kg^{-1}]	Maximal amount [mg kg^{-1}]
Black tea	12	3.21±0.17	9.25±0.42
Green tea	5	3.54±0.12	5.52±0.15
Fruit tea	16	2.71±0.13	27.7±0.9
Coffee beans	10	7.57±0.26	17.5±0.5
Instant coffee	5	13.3±0.4	21.3±0.7

4.3. Analysis of tea and coffee samples

The direct determination of boron in hot water extracts of black, green and fruit teas, roasted coffee beans and instant coffees was carried out. Each sample was extracted twice; each extract was measured five times at spectral line B I 249.773 nm and B I 249.678 nm. The minimal and maximal amount for these samples are summarised in Table 2.

5. Conclusion

The method of determination of boron by ICP–AES considering a possible correction of matrix effect was applied to analyses of hot water extracts of tea and coffee samples (the same way of sample preparation as a routine culinary tea or coffee making). During the hot water treatment, other accompanying elements and substances were leached out, but their extracted amounts were low and did not affect results of boron determination. The efficiency of hot water extraction of boron was about 30–50%. The accuracy of the study was determined by using the Chinese reference material GBW 07605 Tea.

This investigation into the boron content of black, green and fruit teas, roasted coffee beans and instant coffees has established the mean and ranges of boron in 33 tea samples and 15 coffee samples. The mean extracted amount of boron ranged from 3.21±0.17 to 9.25±0.42 mg kg^{-1} in black teas, from 3.54±0.12 to 5.52±0.15 mg kg^{-1} in green teas, from 2.71±0.13 to 27.7±0.9 mg kg^{-1} in fruit teas, from 13.3±0.4 to 21.3±0.7 mg kg^{-1} in instant coffees, from 7.57±0.26 to 17.5±0.5 mg kg^{-1} in roasted coffee beans. The uncertainty of estimates based on recovery data and duplicate analyses varied by up to ±10% for boron and all the other elements determined.

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