Talanta 133 (2015) 127–133

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

An automatic, vigorous-injection assisted dispersive liquid–liquid microextraction technique for stopped-flow spectrophotometric detection of boron

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ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form
30 March 2014
Accepted 21 April 2014
Available online 22 July 2014

Keywords:
Automation
Dispersive liquid–liquid microextraction
Boron
Water
Stopped-flow principle
Flow batch

ABSTRACT

A novel automatic vigorous-injection assisted dispersive liquid–liquid microextraction procedure based on the use of a modified single-valve sequential injection manifold (SV-SIA) was developed and applied for determination of boron in water samples.

The major novelties in the procedure are the achieving of efficient dispersive liquid–liquid microextraction by means of single vigorous-injection (250 μL, 900 μL s^{-1}) of the extraction solvent (*n*-amylacetate) into aqueous phase resulting in the effective dispersive mixing without using dispersive solvent and after self-separation of the phases, as well as forwarding of the extraction phase directly to a Z-flow cell (10 mm) without the use of a holding coil for stopped-flow spectrophotometric detection. The calibration working range was linear up to 2.43 mg L^{-1} of boron at 426 nm wavelength. The limit of detection, calculated as 3*s* of a blank test ($n=10$), was found to be 0.003 mg L^{-1}, and the relative standard deviation, measured as ten replicable concentrations at 0.41 mg L^{-1} of boron was determined to be 5.6%. The validation of the method was tested using certified reference material.

1. Introduction

Boron is an essential nutrient for normal growth of higher plants [1]. It is possible to find numerous reviews devoted to the chemistry, occurrence and health effects of boron [2–4]. Concentrations of boron in natural water can vary in relatively wide ranges. According to World Health Organisation (WHO), the tolerable daily intake for human consumption must be limited up to 0.16 mg of B per kg body weight (bw) per day (d) [5]. Despite the great variety of methods already existing in analytical chemistry for the determination of boron [2,3], this element is still considered to be relatively difficult to determine. That is why it has been said that "Boron is a hard analytical element" [4].

Spectrophotometry, through the use of the colorimetric reaction of boron with reagents such as carminic acid [6] or azomethine-*H* [7], has been frequently used for the determination of boron [2–4]. Other methods which have also been used include spectrofluorimetry, in which the fluorescence intensity of the boron-reagent complex (e.g. resacetophenone) is measured [8], and potentiometry [9], which employs selective electrodes to measure the potentiometric activity of boron in the form of fluoroborate [10] or boric acid [11]. Application of atomic emission spectrometry is limited by interferences [12]; however, some preconcentration techniques have been developed to avoid this problem [13]. Inductively coupled plasma atomic emission spectrometry (ICP-AES) [14] and electrothermal atomic absorption spectrometry [15] are used frequently for determination of boron; however they also could suffer from several problems [3]. Inductively coupled plasma mass spectrometry can provide better sensitivity in comparison with ICP-AES [3,16] or spectrophotometric methods [17], but the high-costs are involved for employing of ICP techniques, therefore many researchers tend to use economically friendly variants [3].

The application of the principles of Green Analytical Chemistry [18] is becoming more and more evident in analytical chemistry

Abbreviations: SV-SIA, Single-valve sequential-injection analysis; DV-SIA, Dual-alve sequential-injection analysis; EC, Extraction cell; MPVTI, 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3*H*-indolium reagent; HC, Holding coil; RT, Reaction tube; SV, Selection valves; SP_1, SP_2, Syringe pumps; InT, Inlet tube; OT, Outlet tube; IT_1, IT_2, Injection tubes

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http://dx.doi.org/10.1016/j.talanta.2014.04.095
0039-9140/

[19].We can observe two such trends in sample pre-treatment, in miniaturisation and automation. One efficient strategy for implementing both of these trends into a single analytical procedure can be achieved by employing liquid-phase microextraction (LPME) techniques (e.g. dispersive liquid–liquid microextraction, DLLME) together with flow analysis, which has recently become an important area of investigation [20]. However, several difficulties can occur in the coupling of LPME/DLLME and sequential injection analysis. The biggest problem appears when organic and aqueous phase are used within the same tubing system; this can result in the formation of a segmented organic film stuck to the inner walls of the tubing due to the different affinity for the PTFE material. Another drawback is the formation of bubbles due to the mixing of aqueous and organic phases, again within the same tubing system. The above-mentioned problems could cause the transport of the bubbles into flow cell during measuring step, which is manifested as artefacts in the analytical signal and non-reproducible results. One solution based on a dual-valve sequential injection manifold (DV-SIA) employing two separate SIA units connected with the extraction chamber by a tubing system was reported [21–23]. The SV-SIA manifold recently suggested by our lab [24] provides another conception in that it allows the entire procedure to be carried out in a single SIA unit.

Another disadvantage in case of DLLME (in both manual and automatic procedures) emerges also with application of dispersive solvent, which can decrease the partition coefficient of analytes [25]. Therefore, the alternative DLLME approaches, which employ the kinetic energy to ensure a mass transfer of analyte into extraction phase have been recently developed [25–27]. To the best of our knowledge, there are only few flow-based DLLME protocols, in which disperser was replaced by kinetic energy, namely air-bubbling [22,24] and magnetic-stirring [28,29].

In this work, the suggested system has been innovated in certain aspects to completely overcome mentioned difficulties. The benefits arising from this approach can be summarised as follows:

1. The peripheral syringe pump, connected directly to the bottom part of the *Extraction Chamber* (EC), offers automatic vigorous-injection of the solvent into the aqueous phase, enabling efficient mixing of the phases and resulting in large mass transfer of analyte into extraction phase without using of dispersive solvent.
2. No additional instruments or homemade devices are required and no special conditions or additional steps, such as magnetic stirring [28,29], heating/cooling [30,31] or microcolumn retention/elution [32–37] are needed.
3. Since a peripheral syringe pump is used for handling the extraction solvent, no contact area remains between the organic and aqueous phases within the same tubing system before measurement.
4. Connecting the EC directly to the Z-flow cell by a short (5 cm) PTFE tube allows easy forwarding of the extraction phase by water as carrier for the monitoring without the use of a holding coil. The suggested delivering technique readily enabled detection step based on stopped-flow principle.
5. Extraction by air-bubbling, used as kinetic energy for assisted microextraction in previous works [22,24], is replaced by vigorous-injection of extraction solvent into the aqueous phase; this reduces the time for automatic assay (250 s) by 100 s when comparing with previous SV-SIA concept (350 s).

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and double-distilled water was used throughout the experiment. The various working solutions of boron were prepared daily from 5×10^{-3} mol L^{-1} of H_3BO_3 stock solution. A 5×10^{-3} mol L^{-1} solution of 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3*H*-indolium reagent (MPVTI) was prepared by dissolving its precise amount in 2 mL of methanol (Centralchem, 99.9% purity) and refilling with water to obtain the required concentration. Xylene (Centralchem, 99.7% purity), toluene (Centralchem, 99.9% purity), *n*-amylacetate (Merck, ≥98% purity) and isobutyl acetate (Sigma-Aldrich, 99% purity) were used as the extraction solvents.

2.2. System arrangement

2.2.1. Off-line set-up

An aliquot of sample solution was transferred into a 10 mL *Reaction Tube* (RT) with a conical bottom, and 0.5 mL of 3 mol L^{-1} H_2SO_4, 0.6 mL of 0.5 mol L^{-1} NaF and water up to a total volume of 2 mL were added. The tube was capped and immersed in an ultrasonic cleaning bath UCI-150 (Trade Raypa, Spain) for boron conversion. After 10 min ultrasonication, the solution was refilled with water to achieve the final volume of 4 mL. The RT containing tetrafluoroborate was then connected to a sequential injection manifold through port 4 of the selection valve in order to perform the subsequent steps (see Section 2.2.2.).

2.2.2. Automatic set-up

For the automated flow-batch procedure, a FIAlab® 3500 sequential injection apparatus (FIAlab® Instrument Systems Inc., Bellevue, USA) was employed (Fig. 1). It is composed of a multi-positional Cheminert selection valve (SV) equipped with eight lateral ports (Valco Instrument Co., Houston, USA) and an integrated syringe pump (SP_1) equipped with 5 mL capacity Carvo glass barrel micro-syringe. The SV was used for automated redirection of reagents by means of a tubing system (all tubes were 20 cm in length, 0.75 mm of i.d.) connected with waste (port 1), air (port 2), water (port 3), BF_4^- (port 4), MPVTI (port 5) and methanol (port 6). SP_1 was used to handle reagents and connected via a holding coil (HC, 2000 cm of length, 1.5 mm of i.d) to the central port of the SV.

The *Extraction Chamber* (EC) was built from a 1.5 mL micro-centrifuge polypropylene tube with a conical bottom and a snap-on cap (1 cm wide, 3.8 cm high) and used to carry out DLLME and self-separation of the aqueous and organic phases. The upper part of the EC was directly connected through an *Inlet Tube* (InT) with an optical Z-flow cell ($l=10$ mm) without the use of a HC. The Z-flow cell was opened into a waste vial through an *Outlet Tube* (OT). It is recommended having both the InT and the OT as short as possible (5 cm long in this work) in order to perform an easy direct forwarding of the extraction phase and to ensure appropriate rinsing of the Z-flow cell during the cleaning procedure. The bottom part of the EC was connected to port 7 of the SV through an *Injection Tube 1* (IT_1, 5 cm in length) and to a peripheral syringe pump (SP_2, MicroCSP-3000, FIAlab® Instruments, Bellevue, USA) equipped also with the 5 mL capacity micro-syringe, through the *Injection Tube 2* (IT_2, 10 cm in length). SP_2 was employed for vigorous-injection of solvent into the aqueous phase.

A DH-2000 (215–2000 nm) deuterium tungsten halogen lamp (Ocean Optics Inc., Dunedin, USA) was used as a light source, and a fibre optic CCD USB 2000 (Ocean Optics Inc., Dunedin, USA) was used as the detector. FIAlab® software was applied as the operating programme, enabling control of the protocol.

2.3. Operational protocol

The procedure begins with the aspiration of water from the reservoir to SP_1. Afterwards, the reagents are aspirated to the HC in the following order: air, water, BF_4^- and MPVTI. The entire content

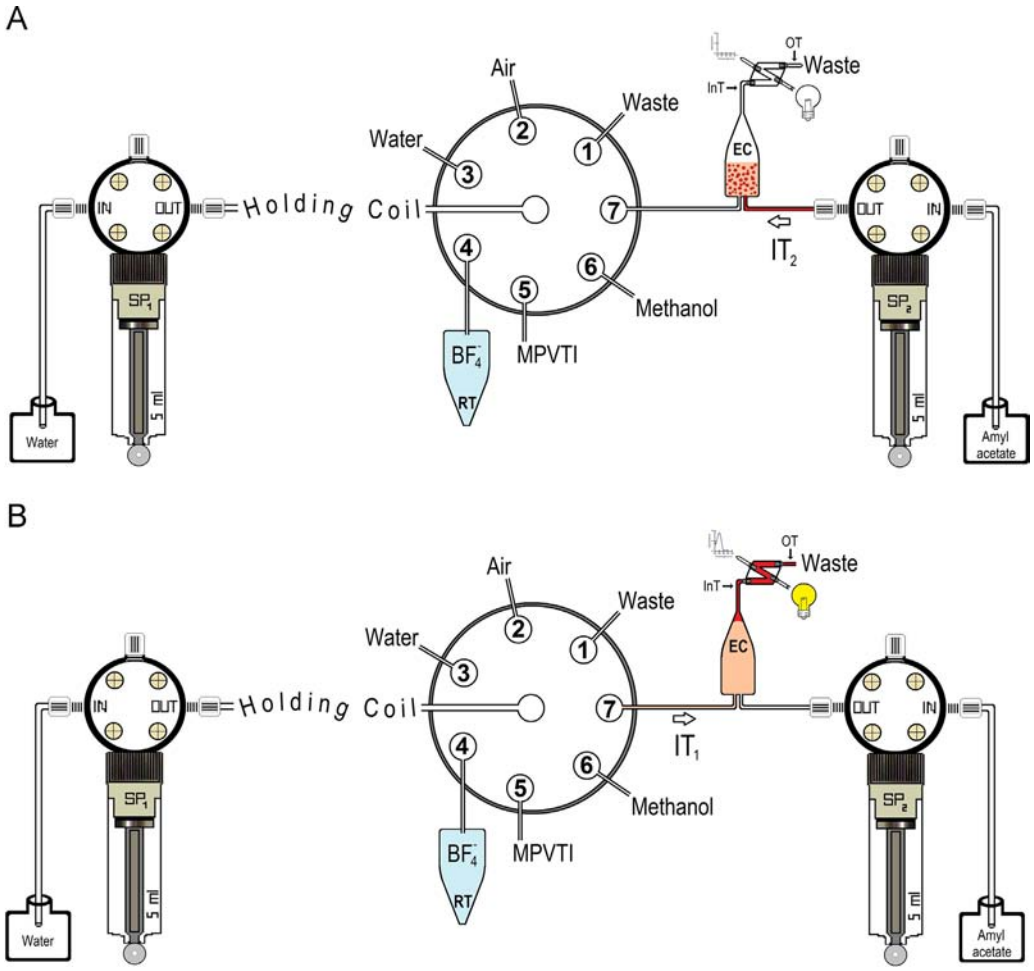

Fig. 1. The suggested set-up for automatic vigorous-injection assisted dispersive liquid–liquid microextraction (A) and direct forwarding of extraction phase (B), SP_1, SP_2, Syringe pumps; HC, Holding coil; MPVTI, 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3*H*-indolium reagent; RT, Reaction tube; EC, Extraction chamber; IT_1, IT_2, Injection tubes; InT, Inlet tube; OT, Outlet tube.

is then pushed towards the EC and followed by air mixing. In the next step, SP_2 is employed for a single vigorous-injection of extraction solvent into the EC at a high flow-rate, resulting in dispersion of the extraction solvent in the aqueous phase (Fig. 2A). Consequently, the transfer of the analyte from the aqueous sample into the tiny droplets of organic solvent takes place in this step. After self-separation of the phases, the water is slowly pumped into the EC through IT_1, resulting in a direct forwarding of the extraction phase lighter than water into the Z-flow cell through the InT for stopped-flow spectrophotometric detection at 426 nm wavelength (Fig. 2B). This solution is similar to the one reported by Anthemidis for on-line micro-volume introduction of an extraction solvent of density lower than water into a flame atomic absorption spectrometery instrument [38]. The stopped-flow mode was carried out by automatically stopping the stream of propelled extraction phase each time at the exact moment, when the Z-flow cell was full. Since no aspiration of extracted product back into holding coil is needed and simple pushing of extraction phase through short PTFE tube (5 cm) is realised by means of water as carrier, the undesirable dispersion of analyte into solvent carrier is completely prevented and therefore increasing of signal response could be obtained. In order to prevent any cross-contamination, the final step includes the complete cleaning of the system by double washing of the EC with a mixture of water and methanol and the rinsing of the Z-flow cell with 750 μL of *n*-amylacetate propelled by means of water as carrier (Supporting information data). The key steps of the entire automatic assay with all of the necessary information are displayed in Table 1.

2.4. Water samples

Tap water from our laboratory was allowed to run for five minutes and was freshly collected into a plastic bottle, from which it was immediately analysed by the suggested procedure without filtration or any other treatment. Bottled spring water was bought in a local supermarket and stored at room temperature before use. Three types of mineral water samples with a natural content of boric acid were brought from different springs in the Transcarpathian region (Ukraine) and also stored in the dark at room temperature. Once opened, all of the mineral water samples were firstly degassed in an ultrasonic bath for 30 min and subsequently analysed.

3. Results and discussion

The determination of boron comprises two separated stages [39]. These are (1) the conversion of boric acid to tetrafluoroborate anion and (2) the formation of ion associate between BF_4^- and MPVTI, followed by DLLME. The reaction chemistry may be

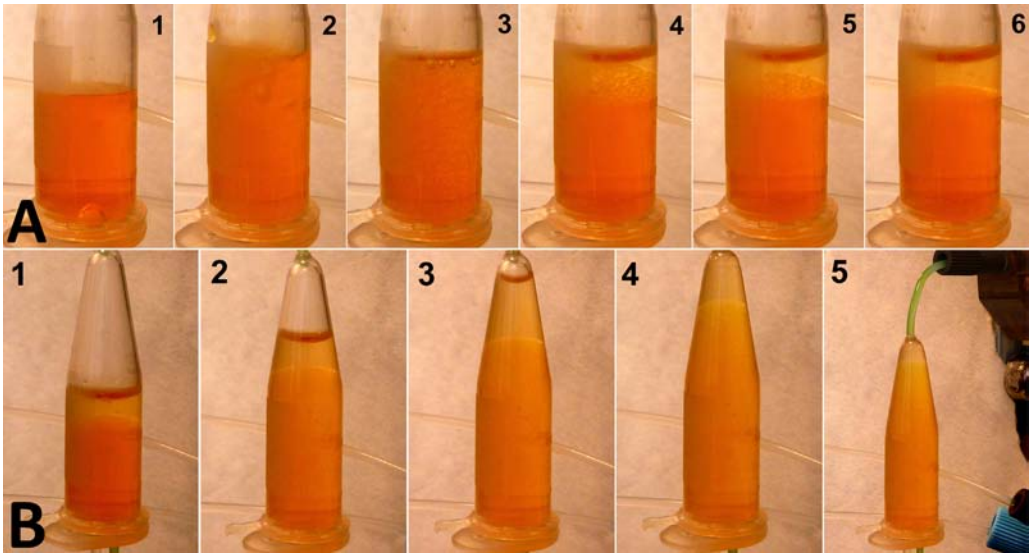

Fig. 2. Photo series for suggested automatic vigorous-injection assisted dispersive liquid–liquid microextraction. (A) Vigorous-injection of solvent into aqueous phase and after self-separation of the phases accomplished in 30 s. (B) Forwarding of the extraction phase directly to a Z-flow cell for stopped-flow spectrophotometric detection.

Table 1
Key steps of operational protocol for the suggested automatic set-up and determination of boron after BF_4^- conversion.

Step	Selection valve	Syringe pump	Status	Flow-rate (μL s^{-1})	Volume (μL)	Operation	Comment
1	–	SP_1	In	1000	1500	Aspirate	Water into SP_1
2	2	SP_1	Out	30	120	Aspirate	Air into HC
3	3	SP_1	Out	30	250	Aspirate	Water into HC
4	4	SP_1	Out	30	600	Aspirate	BF_4^- into HC
5	5	SP_1	Out	30	150	Aspirate	MPVTI into HC
6	6	SP_1	Out	30	1000	Dispense	Reagents into EC
7	2	SP_1	In	200	1000	Aspirate	Air into EC for mixing of reagents
	7		Out	1000		Dispense	
8	–	SP_2	In	100	250	Aspirate	Amyl acetate into EC for DLLME
			Out	900		Dispense	
9	–	–	–	–	–	Delay	30 s for self-separation of both phases
10	1	SP_1	Out	100	400	Dispense	Rest of air into waste
11	7	SP_1	Out	30	985	Dispense	Extraction phase into Z-flow cell for stopped-flow spectrophotometric detection by means of carrier
12	6	SP_1	Out	150	500	2 × Aspirate	Methanol into to HC
	3				1300		Water into HC
13	7	SP_1	Out	200	1800	2 × Dispense	Mixture of water and methanol to wash EC
14	7	SP_1	Out	150	2300	Aspirate	Empty EC
	1				2500	Dispense	Content of EC to waste
15	–	SP_2	InOut	100	750	Aspirate	Amyl acetate from reservoir
						Dispense	Amyl acetate to EC
16	7	SP_1	Out	150	1830	Dispense	Amyl acetate by means of water into EC to clean Z-flow cell
17	7	SP_1	Out	100	2300	Aspirate	Water and Amyl acetate into HC in order to empty EC
18	1	SP_1	Out	200	–	Empty	Clean HC

expressed by the following scheme:

$$H_3BO_3 + 4F^- + 3H^+ = BF_4^- + 3H_2O \quad (1)$$

$$BF_{4(aq)}^- + (MPVTI)_{(aq)}^+ + nS_{(org)} = [BF_4]^-(MPVTI)^+ \times nS_{(org)} \quad (2)$$

Based on the results obtained from the optimisation of various concentrations, the most appropriate conditions for boron conversion were found to be 0.75 mol L^{-1} H_2SO_4 (studied from 0.15 to 1.95 mol L^{-1}) (Fig. 3A) and 0.15 mol L^{-1} NaF (studied from 0.025 to 0.35 mol L^{-1}) (Fig. 3B). The proper concentration of MPVTI for ion associate formation was found to be 7.5×10^{-5} mol L^{-1} (studied from 0.75×10^{-5} to 7.5×10^{-5} mol L^{-1}) (Fig. 3C).

3.1. Study of ultrasonication time

Ultrasonic energy offers a better solution for accelerating the process of boron conversion to BF_4^- than heating [40], as was shown in our previous studies [39,41]. The effect of ultrasonication time was investigated within the range of 4–13 min. A maximum and constant analytical response was achieved within a time interval of 10–13 min. Therefore, 10 min was chosen for further experiments.

3.2. Choice of extraction solvent type and volume

Xylene, benzene, amylacetate and isobutylacetate were tested as extraction solvents. Based on the results presented in Fig. 3D, we

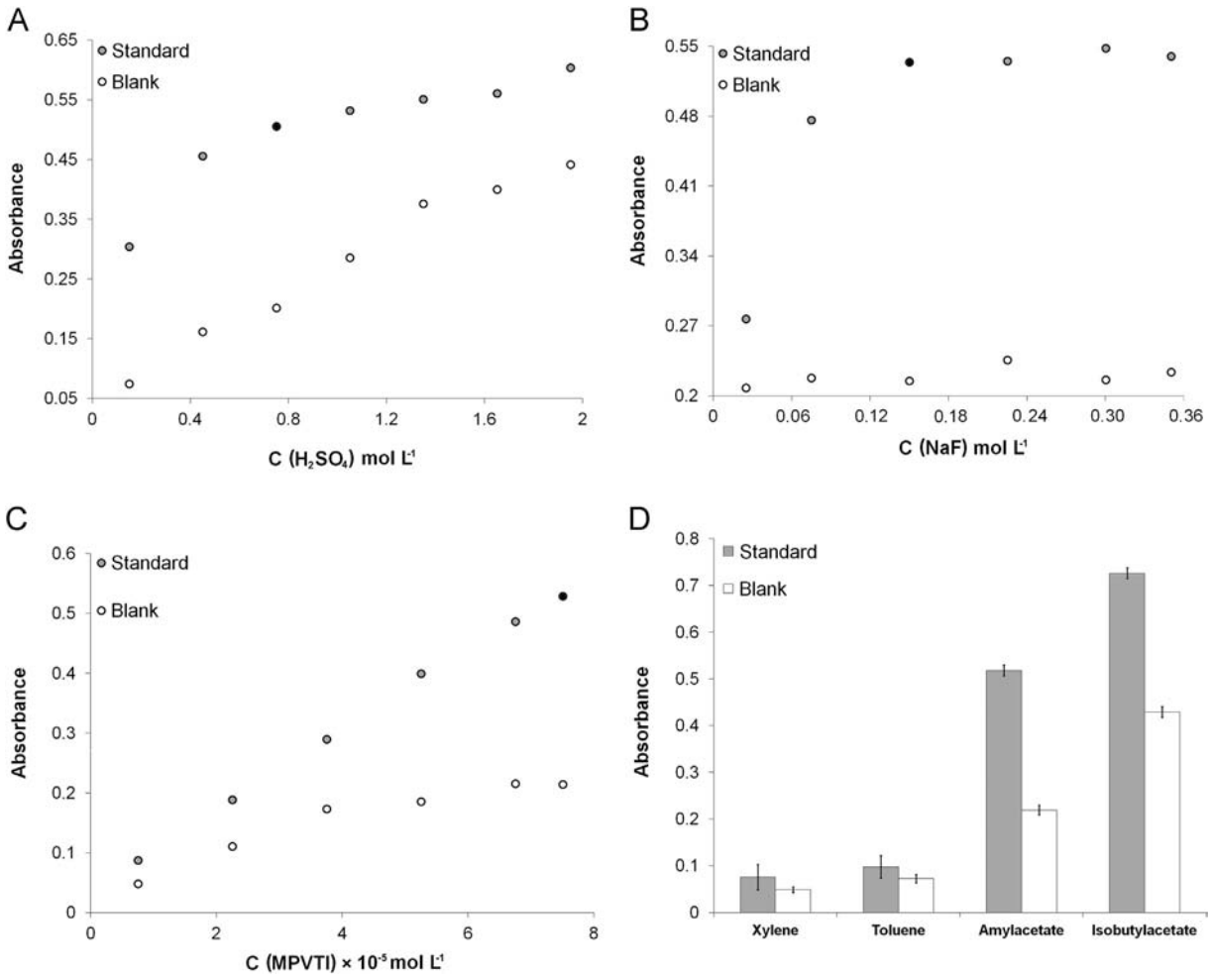

Fig. 3. Investigation of appropriate conditions and effect of extraction solvent type ($n=3$), 0.81 mg L^{-1} of boron; 1.0 mL of aqueous phase; 0.25 mL of organic phase; $l=10$ mm; $\lambda=426$ nm. (A) Effect of H_2SO_4, 0.15 mol L^{-1} of NaF; 7.5×10^{-5} mol L^{-1} of MPVTI. (B) Effect of NaF, 0.75 mol L^{-1} of H_2SO_4; 7.5×10^{-5} mol L^{-1} of MPVTI. (C) Effect of MPVTI, 0.15 mol L^{-1} of NaF; 0.75 mol L^{-1} of H_2SO_4. (D) Effect extraction solvent type, 0.15 mol L^{-1} of NaF; 0.75 mol L^{-1} of H_2SO_4; 7.5×10^{-5} mol L^{-1} of MPVTI. *Calculated for 2 mL aqueous phase in reaction tube (RT).**Calculated for 1 mL aqueous phase in extraction chamber (EC).

selected amylacetate for use in further experiments. A compromise needs to be made between the requirements of green analytical chemistry, which includes the use of least amount of solvent possible and the use of ample volume of extraction solvent for completely filling the Z-flow cell. Thus, the volume of extraction phase was tested from 100 to 400 μL. From the results obtained, 250 μL was taken as the optimal volume in further experiments.

3.3. Study of the extraction process

A single, automatic vigorous-injection of extraction solvent into the aqueous phase at a high flow-rate ensures effective mixing of the solution, resulting in dispersion of the extraction solvent into the aqueous phase. Consequently, due to the large interface area between both phases, the analyte from the aqueous sample is massively transferred into the tiny droplets of organic solvent in this stage. No additional steps are needed to achieve efficient mixing. The study of the flow-rate, depicted in Fig. 4, shows a linear increase in the analytical response depending on the increased velocity of the solvent injection, which indicates proportional intensification of extraction efficiency of extracted product. When using flow-rate higher than 900 μL s^{-1}, we observed a

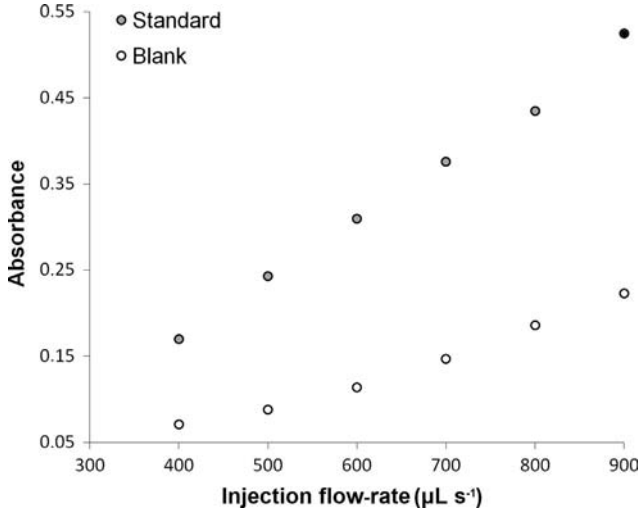

Fig. 4. Study of extraction process by vigorous-injection of solvent into aqueous phase ($n=3$), 0.81 mg L^{-1} of boron; 0.15 mol L^{-1} of NaF; 0.75 mol L^{-1} of H_2SO_4; 7.5×10^{-5} mol L^{-1} of MPVTI; 1.0 mL of aqueous phase; 0.25 mL of organic phase; $l=10$ mm; $\lambda=426$ nm.

forcing of extraction phase into upper part of the EC resulting in blocking of InT entrance. Therefore, 900 μL s^{-1} was chosen as being most suitable for further experiments.

In this work, the difference in densities of aqueous and organic phase is used for their self-separation. No retention in a micro-column and consequently no elution are required. The delay time necessary for phase self-separation after DLLME was investigated in the range from 10 to 100 s. From the results observed, we decided on 30 s as being appropriate for this work.

3.4. Study of interferences

The influence of ions typically present in water samples with boron on the determination of 0.81 mg L^{-1} of boron was examined using model samples and the suggested method. Tolerable recovery was considered to be an error which did not exceed ± 5%. The obtained results showed that the following ions can be tolerated: Cu^{2+} and Co^{2+} at up to 10-fold excess; Mn^{2+} and Zn^{2+} at up to 20-fold excess; Ni^{2+} at up to 30-fold excess; Li^{+} and Fe^{2+} at up to 40-fold excess; NO_3^- and Al^{3+} at up to 60-fold excess; Cl^-, Ca^{2+} and Mg^{2+} at up to 100-fold excess and HCO_3^- at up 2000-fold excess.

3.5. Analytical performance and real sample analysis

The instrumental calibration plot obeyed Beer's law up to 2.43 mg L^{-1} (Supporting information data), with a correlation coefficient (r^2) of 0.9987. The regression equation of the calibration working range was $A=0.331C+0.0169$, where A is the absorbance and C is the concentration of boron at mg L^{-1} in aqueous phase. The limit of detection (LOD), calculated on the basis of 3s criterion $n=10$, was found to be 0.003 mg L^{-1}. The relative standard deviation (RSD), evaluated by measuring 10 replicate determinations of boron at a concentration level of 0.41 mg L^{-1}, was found to be 5.6%. The evaluated parameters are in good comparison with those published in previous studies (Table 2). The suggested automatic assay was realised in 250 s for single sample injection.

Validation of the method was assessed by analysing certified reference material: *WasteWatR™ Boron*, P204-919 (purchased from ERA – A water company, Arvada, Colorado, USA). The results showed no significant differences between the determined and the certified values, with relative standard deviation of 1.6%.

Table 3
Analysis of spiked water samples ($n=4$).

Sample	Added boron[a] (mg L^{-1})	Found boron[a] (mg L^{-1})	RSD (%)	R (%)
Tap water	0	–	–	–
	0.41	0.40 ± 0.01	5.0	97.6
Spring water	0	–	–	–
	0.41	0.41 ± 0.01	2.4	100.0
Mineral water 1[b]	0	0.63 ± 0.01	3.5	–
	0.2	0.83 ± 0.02	4.8	100.0
Mineral water 2[b]	0	1.30 ± 0.02	2.6	–
	0.41	1.69 ± 0.02	1.8	98.8
Mineral water 3[b]	0	0.65 ± 0.02	5.1	–
	0.81	1.44 ± 0.03	4.2	98.6

[a] $\bar{x} \pm (ts/\sqrt{n})$ ($t=3.182$, $P=0.95$); t, Student coefficient for $n-1$ degrees of freedom.
[b] Water with natural content of boric acid.

Table 2
Comparison of the suggested procedure with previously reported flow based UV–vis methods for boron determination.

Flow technique	Product form	Reagent	Wavelength (nm)	RSD (%)	LOD (μg L^{-1})	Linear range (mg L^{-1})	Analysis time/ throughput	Real samples	Ref.
CFA	Steady-state	Azomethine-H	410	n.s.	n.s.	1–10	n.s.	Plant tissue	[42]
CFA	Steady-state	Carminic acid–Sulphuric acid	610	n.s.	20	0.05–3	10 h^{-1} sampling rate	Sawage Sawage effluents River Water	[43]
CFA	Steady-state	Azomethine-H	420	n.s.	n.s.	n.s.	n.s.	Aqueous solutions	[44]
CFA	Steady-state	Azomethine-H	410	± 10	100	Up to 4	n.s.	Raw and Waste water	[45]
FIA	Kinetic	Azomethine-H	420	< 1	n.a.	0.1–6	60 h^{-1} sampling rate	Plants	[46]
MCFA	Steady-state	Azomethine-H	420	1.4	20	Up to 4	120 h^{-1} sampling rate	Plants	[47]
FIA	Kinetic	Azomethine-H	420	n.a.	n.a.	n.a.	25 h^{-1} sampling rate	Soils	[48]
FIA	Kinetic	n.a.	n.a.	3	8	0.04–6	15 h^{-1} sampling rate	Light and heavy water	[49]
FIA	Kinetic	Brilliant green	640	2.6	n.s.	Up to 0.16	n.s.	Silicate rocks	[50]
MSFA	Steady-state	Azomethine-H	420	< 3	n.s.	Up to 5	120 h^{-1} sampling rate	Plants	[51]
FIA	Kinetic	Mannitol containing Bromocresol Green	616	0.7	20	1–30	n.s.	Ceramic materials	[52]
MFA	Kinetic	Azomethine-H	420	2.5	470	Up to 6	48 h^{-1} sampling rate	Plants	[53]
CFA	Steady-state	Azomethine-H	420	2.6	50	Up to 50	33 h^{-1} sampling rate	Soil and plants	[54]
MSFIA	Kinetic	Azomethine-H	420	< 1.4	50	0.2–4	200 s for flow assay	Soil extracts	[55]
MSFB	Steady-state	Azomethine-H	420	n.s.	8	0.1–1	120 h^{-1} sampling rate	Plants	[56]
FB (SIA)	Steady-state	MPVTI	426	5.6	3	Up to 2.43	250 s for flow-batch assay	Natural water	This work

FIA, Flow injection analysis; MCFA, Monosegmented continuous flow analysis; MSFA, Monosegmented flow analysis; MFA, Multicommutation flow analysis; CFA, Continuous flow analysis; MSFIA, Multisyringe flow injection analysis; MSFB, Monosegmented flow-batch analysis; SIA, Sequential injection analysis; FB (SIA), SIA instrument was employed to perform automatic flow-batch procedure; MPVTI, 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3*H*-indolium reagent; n.a., the full text is not available; n.s., not specified.

The suggested procedure was applied for the determination of boron in spring and tap water without boric acid and three mineral water samples with a natural content of boric acid. The results (Table 3) showed satisfactory recoveries, with an average value of 99%, indicating suitability of the method for determination of boron in water samples.

4. Conclusion

A previously reported SV-SIA manifold [24] has been modified and improved in certain aspects and applied for novel automatic vigorous-injection assisted dispersive liquid–liquid microextraction and stopped-flow spectrophotometric determination of boron in real water samples. The main difference in the procedure lies in the employment of a peripheral syringe pump for handling the organic phase, while no other additional parts are used in comparison with the SV-SIA. The modifications enable (1) the automatic vigorous-injection of solvent into the aqueous phase to ensure efficient mixing of the phases; (2) contact between the organic and aqueous phases within a single tubing system to be eliminated; (3) easy direct-forwarding of the extraction phase for the detection step without the use of a holding coil; (4) simple cleaning of the whole system. In comparison with previously reported works, no additional instruments or homemade devices are required, and no special conditions or additional steps, such as magnetic stirring [28,29], heating/cooling [30,31], mixing by air bubbling [22,24] or microcolumn retention/elution [32–37] are needed. The suggested approach also satisfies the requirements of environmentally and user-friendly chemistry, since it employs low amounts of organic solvents and all parts of the manifold are commercially available. And it can be easily adapted for the elaboration of procedures used to determine other analytes extractable by organic solvents.

Acknowledgements

V. Andruch gratefully acknowledges the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences (VEGA 1/1096/12) for partial financial support. M. Alexovič would like to thank to International Visegrad Fund for providing a five-month scholarship. This work was supported in part through the development of bilateral cooperation between Slovak and Poland universities within the Operational Programme Education financed by the European Social Fund (ESF) (Project ITMS 26110230084).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.04.095.

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