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A dispersive liquid–liquid microextraction procedure for determination of boron in water after ultrasound-assisted conversion to tetrafluoroborate

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ABSTRACT

A novel, simple and green procedure is presented for the determination of boron. The method is based on ultrasound-assisted conversion of boron to tetrafluoroborate anion and the formation of an ion pair between BF_4^- and Astra Phloxine reagent (R), followed by dispersive liquid–liquid microextraction of the ion pair formed and subsequent UV–vis spectrophotometric detection. The conversion of boron to tetrafluoroborate anion is performed in an acidic medium of 0.9 mol L^{-1} H_2SO_4 in the presence of 0.1 mol L^{-1} F^- by means of 10 min of ultrasonication. The extraction of the ion pair formed between BF_4^- and R (1×10^{-4} mol L^{-1} R) is carried out by dispersive liquid–liquid microextraction using 0.5 mL of amyl acetate (as extraction solvent), tetrachloromethane (as auxiliary solvent) and acetonitrile (as dispersive solvent) in a ratio of 1:1:2. The absorbance of the coloured extracts obeys Beer's law in the range 0.22–18.7 mg L^{-1} of B(III) at 553 nm wavelength. The limit of detection calculated from a blank test ($n = 10$) based on 3 s is 0.015 mg L^{-1} of B(III). The method was applied to the determination of boron in mineral waters.

1. Introduction

Recent years have seen a growing interest in "green chemistry". Unfortunately, analytical chemistry was, until recently, an exception [1]. Armenta et al. state that the main principles of green analytical chemistry "are to replace toxic reagents, to miniaturize and to automate methods, making it possible to reduce dramatically the amounts of reagents consumed and wastes generated, so reducing or avoiding side effects of analytical methods" [1]. We have previously published articles devoted to automation and miniaturisation of analytical procedures which describe a novel dual-valve sequential injection manifold (DV-SIA) for automated liquid–liquid extraction (LLE) [2,3], the application of ultrasound as a replacement for heating [4] and the development of novel dispersive liquid–liquid microextraction (DLLME) procedures for the determination of various analytes [5,6].

Although elemental boron has only limited industrial uses, many of its compounds, boric acid and sodium salts of boron in particular, are commonly used in a variety of industries, including the production of herbicides, insecticides and fertilizers and the manufacture of glass, porcelain enamel, ceramic glazes and metal alloys [7–9]. Argust [7] and Howe [10] reviewed the distribution [7] and effects of boron in the environment [10]. According to Kot [11], data on the physiological functions of boron are incomplete and frequently contradictory, and published data are both scarce and vague. He therefore reviewed the most current references on the sources, turnover and speciation of boron in the environment and boron's possible effects on human health. Based on evidence from various laboratories, Nielsen states that boron is a bioactive and beneficial element and that some higher animals require it to complete the life cycle [12]. Parks and Edwards summarized the chemistry, occurrence and health effects of boron, along with the existing regulations and guidelines for boron and different methods for removing it from drinking water [13]. Minoia and co-workers focused on boron's toxicology and health impacts [14,15]. Boron is an essential nutrient for the normal growth of higher plants, and the availability of boron in soil and irrigation water is an important determinant of agricultural production, though if present in excess it becomes toxic for plants [16–19].

Boron exists in natural waters primarily as undissociated boric acid along with some borate ions. Soils and sediments can adsorb waterborne boron, though this process depends on boron concentration and the pH of the water [9]. The natural content of borate in groundwater and surface water is usually quite small, while boron concentration in fresh water depends primarily on the leaching of boron from the surrounding land as well as from industrial and municipal outflows. Boron concentrations in groundwater have a broad range, from less than 0.3 to over 100 mg L^{-1}. Average concentration in the oceans is 4.5 mg L^{-1} and ranges in fresh surface waters from <0.001 to 2 mg L^{-1} [9]. Conventional drinking water

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treatment methods do not typically remove boron from water [9]. According to Council Directive 98/83/EC from 3 November 1998 on the quality of water intended for human consumption, the boron content in drinking water must be no more than 1.0 mg L^{-1} [20].

Boron is a difficult element for analysis [11]. Its analytical chemistry has been discussed in a number of books and reviews [21–23], while variety of methods have been described for boron determination in water samples [22,23], a spectrophotometric method using azomethine-H being the most common utilised. In addition, other methods based on the reaction of boron with a variety of organic reagents have also been suggested. The primary drawbacks of these methods are considered the necessity for separating boric acid through distillation as methyl borate or the need for concentrated sulphuric acid as a reaction medium. As a result, with boron determination special attention must be paid on preventing the escape of volatile boron compounds and contamination of the sample by boron from the glass used in the laboratory. One potential way of developing novel procedures for boron determination could be a method based on the conversion of boric acid to tetrafluoroborate anion followed by ion pair formation with dye reagents and the extraction of the ion pair formed into organic solvent with subsequent spectrophotometric detection [4,21,22,24].

Despite the existence of numerous methods for boron determination, we were unable to find a DLLME procedure for its determination in the literature. The aim of this study was the development of a green procedure for boron determination based on ultrasound-assisted conversion of boron to tetrafluoroborate anion, the formation of an ion pair between BF_4^- and Astra Phloxine reagent, followed by dispersive liquid–liquid microextraction of the ion pair formed and subsequent UV–vis spectrophotometric detection.

2. Experimental

2.1. Reagents

All solutions used were prepared from analytical grade reagents and stored in polyethylene bottles. Ultra pure water from Millipore Milli-Q RG (Millipore, USA) was used throughout the work. A working solution containing 5×10^{-2} mol L^{-1} of boron was prepared by dissolving 0.3092 g H_3BO_3 in water and dilution with water up to a volume of 100 mL. The 1,3,3-trimethyl-2-[3-(1,3,3-trimethyl-1,3-*H*-indol-2-ylidene)propenyl]-3*H*-indolium chloride, more commonly known as dimethylindocarbocyanine dye or Astra Phloxine reagent (R), was obtained from Jiacheng–Chem Enterprises Ltd. (China) and was used without additional purification. A 1×10^{-3} mol L^{-1} aqueous solution of the reagent was prepared by dissolving 0.0785 g of its chloride salt in several droplets of methanol and subsequent dilution with water up to a volume of 200 mL. A 0.5 mol L^{-1} aqueous solution of NaF was used to convert H_3BO_3 to BF_4^-. The pH was set by the addition of 3 mol L^{-1} H_2SO_4. All solvents used were of analytical grade reagents.

2.2. Apparatus

A Cary 100 Bio UV–vis spectrophotometer (Varian Inc., USA) and a Spekol-11 spectrophotometer (Carl Zeiss, Germany) equipped with a matched cell of 1 mm path length were used for spectrophotometric measurements. A Sonorex Digitec ultrasonic compact bath DT 31 (Bandelin Electronic, Germany) was used as source of ultrasonic energy. Centrifugation was carried out using an MPW-310 centrifuge (Mechanika Precyzyjna, Poland).

2.3. Calibration of the method

Various amounts of the boron were put into 10 mL centrifugal tubes. Next, 0.2 mL of 0.5 mol L^{-1} NaF and 0.3 mL of 3 mol L^{-1} H_2SO_4 were added, and the volumes were filled up to 1 mL with water. The solution was thoroughly mixed and then sonicated in an ultrasonic bath for 10 min. Then 3.5 mL water and 0.5 ml of 1×10^{-3} mol L^{-1} Astra Phloxine reagent were added, and the solution was again mixed well. Next, 0.5 mL of a mixture of solvents containing amyl acetate as extraction solvent, CCl_4 as auxiliary solvent and acetonitrile as dispersive solvent in the ratio 1:1:2 (v/v/v) was forcefully injected using a 1 mL glass syringe. The mixture was gently shaken 3 times and then centrifuged at 3000 rpm for 2 min., leaving a layer of sediment containing a mixture of amyl acetate and CCl_4 at the bottom of each tube. This was removed using a Hamilton syringe, inserted into a matched quartz cell, and the absorbance was measured at 553 nm.

2.4. Procedure for real samples

A volume of sample up to 0.5 mL, depending on the anticipated boron content, was placed in a polyethylene test tube. All of the required reagents were then added and the determination carried out as described above in Section 2.3.

3. Results and discussion

A number of investigators have previously studied the conversion of boric acid to tetrafluoroborate anion and its application to boron determination. Their results are summarised in ref. [22]. Thermodynamic calculations for the $(H_3BO_3)–F^-–H^+$ system were carried out by Katagiri et al. [25]. The tetrafluoroborate anion forms best in an acidic medium. However, at pH > 1, this process is slowed due to hydrolysis of BF_4^- and the formation of BF_3OH^-. Such a result is unwanted, however, because the mentioned anion forms compounds with dye reagents not extractable by organic solvents. To adjust the acidity, it is best to use sulphuric acid, because sulphates, unlike the anions of other strong acids, do not form extractable ion pairs with the dye reagents. At acidities which are optimal for conversion, some dye reagents exist in a doubly charged form (HR^{2+}) which is unable to form an ion pair with BF_4^- that is extractable by organic solvents. In addition to the appropriate acidity, an excess of fluoride ions is also needed for the most complete conversion of boric acid to tetrafluoroborate anion. However, a large excess of fluoride anion is also undesirable, because F^- is capable of combining with dye reagents to form compounds which can be extracted by organic solvents. Therefore, conversion in general is performed in a minimal volume at high acidity and with an excess of fluoride ions, though after the conversions, the solution is diluted with water to lower the fluoride concentration, and the value of the pH is adjusted [22]. The application of dye reagents—which have a wide range for their singly charged (R^+) form—such as Astra Phloxine, seems to offer a better solution because the pH can be adjusted through simple dilution, and no buffer solution is required [4]. The conversion of H_3BO_3 into HBF_4 runs relatively slowly, though applying heat speeds up the formation of HBF_4 [24]. We previously reported a method for boron determination in which heating was replaced by ultrasonic irradiation [4] which offers some advantages [4].

3.1. Investigation of the dispersive liquid–liquid microextraction procedure

The majority of detection techniques commonly require the initial separation and/or pre-concentration of analytes. Several methods for the pre-treatment of samples, such as cloud point extraction [26], micelle-mediated extraction [27,28], pressurized LLE [29] and synergistic LLE [30], have appeared in recent literature. Liquid–liquid extraction, which is among the oldest of separation techniques and remains the most commonly utilised, has limitations, however (if manually performed), primarily due to

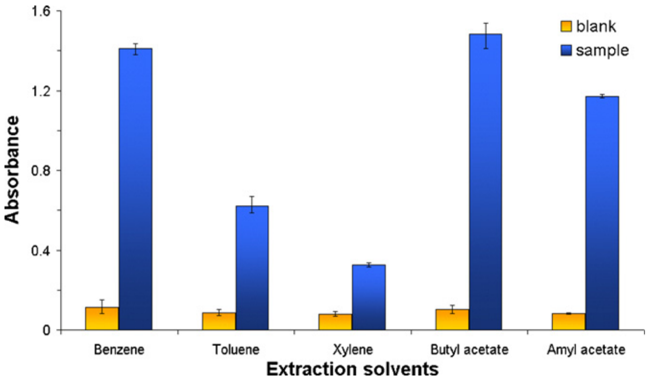

Fig. 1. Effect of the extraction solvent. Conditions for conversion: 1×10^{-3} mol L^{-1} H_3BO_3; 0.9 mol L^{-1} H_2SO_4; 0.1 mol L^{-1} F^-; 10 min sonication in an ultrasonic bath. Conditions for extraction: 1×10^{-4} mol L^{-1} Astra Phloxine; 0.5 mL of a mixture of solvents containing various extraction solvents, tetrachloromethane and acetonitrile in 1:1:2 (v/v/v) ratio, l = 1 mm; λ = 553 nm.

the large volumes of hazardous solvents used [31,32]. As a result, conventional LLE has been replaced in recent years by dispersive liquid–liquid microextraction (originally introduced by Assadi and co-workers [33] in 2006), which has several advantages over LLE [34,35]. The primary advantages lie in the fact that DLLME requires only small amounts of organic solvent and that it shortens extraction time considerably due to the large surface area formed between the aqueous and organic phases. The effects of the nature of the extraction solvent, the auxiliary solvent and the dispersive solvent were studied.

3.1.1. *Effect of the extraction solvent*

The requirements for extraction solvents in a variety of liquid–liquid extraction approaches are well known and have been widely discussed [31,36,37]. They can be summarised as follows: low solubility in water, high efficiency for extraction of the target analyte, and minimum extraction of the blank test [5]. The term for the extraction solvents used in DLLME are the same as for solvents used in conventional LLE [38]. Based on a review of the literature as well as our own experience [4,39–46], it is assumed that the aromatic hydrocarbons and acetic esters are in general the most suitable for extracting ion pairs, because they are usually characterised as being very good for such extractions while simultaneously minimising the extraction of simple dye salts (the blank test). Therefore, various organic solvents (water solubility, g/100 mL) from these groups, such as benzene (0.175), toluene (0.047), xylene (cca. 0.013), amyl acetate (0.2), butyl acetate (2.3), and ethyl acetate (7.9), were tested as extractants. The solubility of the extraction solvent in water is one of the important factors affecting the volume of sedimented phase [47]. Ethyl acetate was thus excluded a priori and was not tested.

A series of experiments were carried out similar to that described in Section 2.3, the difference being that the DLLME procedure was performed using various extraction solvents, and the value of analytical response as well as signal-to-noise ratio were then investigated. Based on the results obtained, which are presented in Fig. 1, seems to be that benzene, amyl acetate and butyl acetate are the best extraction solvents. Benzene was thus excluded because of its toxicity. Due to lower solubility in water, the amyl acetate was chosen for further experiments.

3.1.2. *Effect of the auxiliary solvent*

Since amyl acetate, which was selected as the extraction solvent, has a density lower than that of water, an approach previously reported on from our laboratory [5,6] and based on the application of an auxiliary solvent was used. This method is based on the addition of an auxiliary solvent to the extraction solvent in order to ensure that the resulting mixture of solvents has a density higher than that of water, thus allowing simple phase separation by centrifugation. Solvents with a density significantly higher than that of water, such as dichloromethane, trichloromethane (chloroform), tetrachloromethane, tetrachloroethylene and chlorobenzene, were tested as auxiliary solvents. The choice of auxiliary solvent was based on the maximum signal which simultaneously offered a minimal blank test. It is evident from the experimental results that tetrachloromethane is the best auxiliary solvent, and it was therefore selected for further experiments.

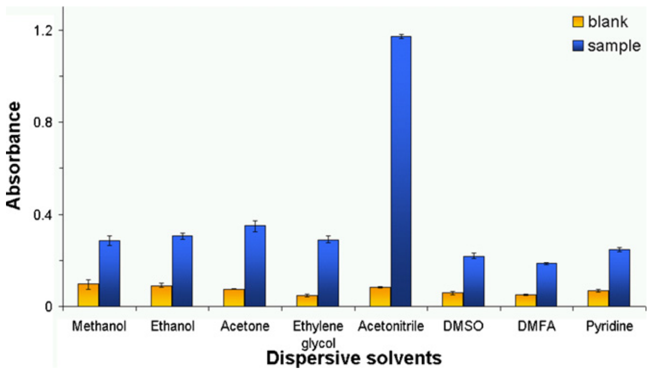

Fig. 2. Effect of the dispersive solvent. Conditions for conversion: 1×10^{-3} mol L^{-1} H_3BO_3; 0.9 mol L^{-1} H_2SO_4; 0.1 mol L^{-1} F^-; 10 min sonication in an ultrasonic bath. Conditions for extraction: 1×10^{-4} mol L^{-1} Astra Phloxine; 0.5 mL of a mixture of solvents containing amyl acetate, tetrachloromethane and various dispersive solvents in 1:1:2 (v/v/v) ratio, l = 1 mm; λ = 553 nm.

3.1.3. *Effect of the dispersive solvent*

The main requirements for a dispersive solvent are its solubility in the extraction solvent and its miscibility with water, so that fine droplets (a cloudy solution) of the extraction solvent can form in the aqueous phase. As a result, methanol, ethanol, acetone and acetonitrile are usually tested as dispersive solvents [47]. A series of experiments were carried out similar to that described in Section 2.3, the difference being that the DLLME procedure was performed using various dispersive solvents (methanol, ethanol, acetone, ethylene glycol, acetonitrile, dimethylsulphoxide (DMSO), *N*,*N*-dimethylformamide (DMFA), and pyridine) and the value of analytical response as well as signal-to-noise ratio were then investigated. Based on the results (Fig. 2), we concluded that acetonitrile is the best dispersive solvent and it was therefore selected for further experiments.

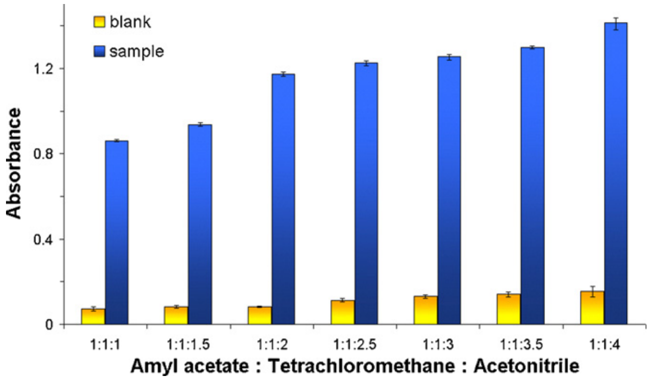

Fig. 3. Effect of solvents ratio. Conditions for conversion: 1×10^{-3} mol L^{-1} H_3BO_3; 0.9 mol L^{-1} H_2SO_4; 0.1 mol L^{-1} F^-; 10 min sonication in an ultrasonic bath. Conditions for extraction: 1×10^{-4} mol L^{-1} Astra Phloxine; 0.5 mL of a mixture of solvents containing amyl acetate, tetrachloromethane and acetonitrile in various v/v/v ratio, l = 1 mm; λ = 553 nm.

Table 1
A comparison of spectrophotometric procedures for boron determination.

Author [Ref]	Year	Extraction solvent	Solvent volume, mL	Linear range, mg L^{-1}	LOD, mg L^{-1}	Sample
Aznarez et al. [48]	1985	2,2,4-Trimethyl-1,3-pentanediol in chloroform	10	0.05–0.4	0.003	Plants, waters
Wimmer and Goldbach [49]	1999	2-Ethyl-1,3-hexanediol in chloroform	0.05	Up to 3	0.018	Waters, plants
Ramanjaneyulu et al. [50]	2008	2-Ethyl hexane 1,3-diol in chloroform	1 (five times)	80–730 ng	12 ng	U–Al–Si alloy
Ramanjaneyulu et al. [51]	2010	2-Ethyl hexane 1,3-diol in chloroform	1 (five times)	0.1–0.8 μg	12 ng	Zr–Nb alloys
Balogh et al. [24]	2009	Benzene	3	0.03–0.55	0.02	Waters
Škrlíková et al. [4]	2010	Amyl acetate	5	0.1–1.0	0.02	Waters pharmaceuticals
This work	2011	Amyl acetate/CCl_4/acetonitrile	0.5	0.22–18.7	0.015	Waters

Table 2
Intra-day and inter-day precision and accuracy data for the determination of boron.

Taken, mg L^{-1}	Intra-day		Inter-day	
	Determined[a], mg L^{-1}	R, %	Determined[a], mg L^{-1}	R, %
2.2	2.1 ± 0.1	95.5	2.1 ± 0.1	95.5
8.8	9.0 ± 0.4	102.3	9.0 ± 0.4	102.3
14.3	14.3 ± 0.2	100.0	14.2 ± 0.2	99.3
17.6	17.5 ± 0.4	99.4	17.3 ± 0.4	98.3

[a] $\bar{x} \pm s\frac{t}{\sqrt{n}}$ ($t = 2.776$, $P = 0.95$), t – Student coefficient for n–1 degrees of freedom; $n = 5$.

3.1.4. Effect of solvents ratio

Besides the effect of the nature of the extraction solvent, auxiliary solvent and dispersive solvent, the effect of the solvents ratio was also studied (Fig. 3). A series of experiments was performed in which the ratio of extraction solvent and auxiliary solvent kept constant at 1:1 (v/v), and the proportion of acetonitrile was altered. Increasing the acetonitrile proportion caused the analytical signal to noise. The maximum analytical signal was obtained using a solvents ratio of 1:1:4 (v/v/v); however, the relative standard deviation of the signal and the value of the blank test were high. The ratio 1:1:2 (v/v/v) was therefore selected for further experiments.

3.2. Figure of merit

Based on the results obtained, a spectrophotometric method for the determination of boron using the DLLME procedure was suggested. The method is based on the reaction of boric acid with fluoride upon ultrasonication and the resulting formation of tetrafluoroborate anion, followed by the dispersive liquid–liquid microextraction of BF_4^- with Astra Phloxine reagent into 0.5 mL of a mixture of solvents containing amyl acetate as extraction solvent, CCl_4 as auxiliary solvent and acetonitrile as dispersive solvent in the ratio 1:1:2 (v/v/v) and subsequent spectrophotometric detection.

Table 3
Effect of foreign ions (4.4 mg L^{-1} H_3BO_3).

Ion	B(III) found, mg L^{-1}	B:interferent ratio	Error, %
Li^+	4.3	1:25	−2.3
	4.2	1:50	−4.5
Na^+	4.6	1:3000	4.5
K^+	4.5	1:500	2.3
Ca^{2+}	4.3	1:50	−2.3
	4.1	1:100	−6.8
Ba^{2+}	4.3	1:10	−2.3
Mg^{2+}	4.3	1:20	−2.3
	4.1	1:50	−6.8
Al^{3+}	4.2	1:20	−4.5
	4.1	1:50	−6.8
Cu^{2+}	4.5	1:10	2.3
Zn^{2+}	4.5	1:20	2.3
Cl^-	4.5	1:1000	2.3
Br^-	4.6	1:50	4.5
SO_4^{2-}	4.3	1:500	−2.3
NO_3^-	4.6	1:100	4.5
Fe^{3+}	4.3	1:20	−2.3

Table 4
Determination of B in mineral waters (MW) ($n = 5$).

Sample	Suggested method, mg L^{-1}	Reference method, mg L^{-1}
MW1	0.56 ± 0.04	0.59 ± 0.02
MW2	2.3 ± 0.2	2.3 ± 0.1
MW3	7.7 ± 0.3	8.0 ± 0.1

A comparison of the developed procedure with other spectrophotometric methods reported in the literature is given in Table 1. The limit of detection (LOD) and linear range of our method and those of other spectrophotometric methods are comparable. The main advantages of the developed procedure are: (1) a much lower consumption of organic solvent and the ensuing reduced generation of wastes in comparison with [4,24,48,50,51]; (2) no need to use benzene in comparison with [24]; (3) the procedure is faster, as no time is needed for colour development [48–51] and no heating is required [24,48].

3.2.1. Calibration range

A calibration plot was constructed from nine data points over a range of concentrations 0.22–18.7 mg L^{-1}. The LOD, calculated based on three times the standard deviation of the blank test ($n = 10$), was found to be 0.015 mg L^{-1} of boron.

3.2.2. Precision and accuracy

The precision and accuracy of the developed method were checked by performing five replicate determinations of boron at four concentration levels over two days and then calculating the relative standard deviation percentage (RSD, %) and the recovery percentage (R, %). The inter-day and intra-day precision and accuracy results are presented in Table 2 and show good repeatability of the suggested method.

3.2.3. Interferences

The effect of diverse ions on the determination of 4.4 mg L^{-1} of boron was studied according to the above-described procedure. Tolerance for an ion was taken as a boron:interferent ratio that caused an error no higher or lower than ±5% (Table 3).

3.2.4. Application of the method

The method was applied to the determination of boron in mineral water samples (Table 4), and the obtained results showed sufficient agreement between the determined values from the suggested and the reference method [52].

4. Conclusion

To the best of our knowledge, a dispersive liquid–liquid microextraction for the determination of boron has been described for the first time. The combination of ultrasound-assisted conversion with a dispersive liquid–liquid microextraction procedure offers some advantages in comparison with previously reported methods for boron determination [4,24]. The main advantages of ultrasonication in comparison with conventional heating [24] are that the conversion process occurs much faster, thus decreasing reaction time, and that it does not lead to the heating of the sample, thus preventing the escape of volatile products formed. The main advantages of DLLME in comparison with conventional LLE [4,24] are the considerable decreasing of the consumption of hazardous organic solvents (thus making the procedure greener) and the significant shortening of the extraction time as a consequence of the large surface area formed between the aqueous and organic phases.

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References

[1] S. Armenta, S. Garrigues, M. de la Guardia, Trends Anal. Chem. 27 (2008) 497–511.
[2] J. Škrlíková, V. Andruch, H. Sklenářová, P. Chocholouš, P. Solich, I.S. Balogh, Anal. Chim. Acta 666 (2010) 55–61.
[3] J. Škrlíková, V. Andruch, H. Sklenářová, P. Chocholouš, P. Solich, I.S. Balogh, Anal. Methods 2 (2010) 1134–1139.
[4] J. Škrlíková, V. Andruch, I.S. Balogh, H. Sklenářová, P. Solich, Anal. Methods 2 (2010) 1275–1279.
[5] L. Kocúrová, I.S. Balogh, J. Škrlíková, J. Posta, V. Andruch, Talanta 82 (2010) 1958–1964.
[6] I.S. Balogh, L. Rusnáková, J. Škrlíková, L. Kocúrová, M. Török, V. Andruch, Int. J. Environ. Anal. Chem., in press, doi:10.1080/03067319.2010.537750.
[7] P. Argust, Biol. Trace Elem. Res. 66 (1998) 131–143.
[8] Toxicological Review of Boron and Compounds, U.S. Environmental Protection Agency, Washington, DC, 2004.
[9] Boron in Drinking-water, Guidelines for Drinking-Water Quality, 2nd ed. Addendum to vol. 2. Health criteria and other supporting information. World Health Organization, Geneva, 1998.
[10] P.D. Howe, Biol. Trace Elem. Res. 66 (1998) 153–166.
[11] F.S. Kot, Rev. Environ. Sci. Biotechnol. 8 (2009) 3–28.
[12] F.H. Nielsen, Nutr. Rev. 66 (2008) 183–191.
[13] J.L. Parks, M. Edwards, Crit. Rev. Environ. Sci. Technol. 35 (2005) 81–114.
[14] C. Minoia, C. Gregotti, A. Di Nucci, S.M. Candura, M. Tonini, L. Manzo, G. Ital. Med. Lav. 9 (1987) 119–124.
[15] C. Locatelli, C. Minoia, M. Tonini, L. Manzo, G. Ital. Med. Lav. 9 (1987) 141–146.
[16] J.J. Camacho-Cristóbal, J. Rexach, A. González-Fontes, J. Integr. Plant Biol. 50 (2008) 1247–1255.
[17] J. Takano, K. Miwa, T. Fujiwara, Trends Plant Sci. 13 (2008) 451–457.
[18] M. Tariq, C.J.B. Mott, Asian J. Plant Sci. 6 (2007) 195–202.
[19] P.H. Brown, N. Bellaloui, M.A. Wimmer, E.S. Bassil, J. Ruiz, H. Hu, H. Pfeffer, F. Dannel, V. Römheld, Plant Biol. 4 (2002) 205–223.
[20] Official Journal of the European Communities, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1998:330:0032:0054:EN:PDF.
[21] W.J. Williams, Handbook of Anion Determination, Butterworths, London, 1979.
[22] A.A. Nemodruk, Z.K. Karalova, Boron, Nauka, Moscow, 1964 (in Russian).
[23] R.N. Sah, P.H. Brown, Microchem. J. 56 (1997) 285–304.
[24] I.S. Balogh, V. Andruch, M. Kádár, F. Billes, J. Posta, E. Szabová, Int. J. Environ. Anal. Chem. 89 (2009) 449–459.
[25] J. Katagiri, T. Yoshioka, T. Mizoguchi, Anal. Chim. Acta 570 (2006) 65–72.
[26] V.A. Lemos, G.T. David, Microchem. J. 94 (2010) 42–47.
[27] D. Kara, Talanta 79 (2009) 429–435.
[28] T. Madrakian, A. Afkhami, A. Mousavi, Talanta 71 (2007) 610–614.
[29] J. Moreda-Pineiro, E. Alonso-Rodríguez, P. López-Mahía, S. Muniategui-Lorenzo, E. Fernández-Fernández, D. Prada-Rodríguez, A. Moreda-Pineiro, A. Bermejo-Barrera, P. Bermejo-Barrera, Anal. Chim. Acta 572 (2006) 172–179.
[30] G.S. Kamble, S.S. Kolekar, S.H. Han, M.A. Anuse, Talanta 81 (2010) 1088–1095.
[31] F. Pena-Pereira, I. Lavilla, C. Bendicho, Spectrochim. Acta Part B 64 (2009) 1–15.
[32] N. Aristidis, Anthemidis, G. Kallirroy-Ioanna, Ioannou, Talanta 80 (2009) 413–421.
[33] M. Rezaee, Y. Assadi, M.-R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1–9.
[34] C. Bosch Ojeda, F. Sánchez Rojas, Chromatography 69 (2009) 1149–1159.
[35] X.-H. Zang, Q.-H. Wu, M.-Y. Zhang, G.-H. Xi, Z. Wang, Chin. J. Anal. Chem. 37 (2009) 161–168.
[36] P.P. Kish, I.S. Balog, B.Ya. Spivakov, Yu.A. Zolotov, Zh. Anal. Khim. 31 (1976) 1114–1123.
[37] I.S. Balog, P.P. Kish, V.V. Bagreev, I.I. Pogoida, Zh. Anal. Khim. 45 (1990) 289–295.
[38] P.X. Baliza, L.S.G. Teixeira, V.A. Lemos, Microchem. J. 93 (2009) 220–224.
[39] T. Prasada Rao, M.L.P. Reddy, A. Ramalingom Pillai, Talanta 46 (1998) 765–813.
[40] I.S. Balogh, V. Andruch, Anal. Chim. Acta 386 (1999) 161–167.
[41] V. Andruch, I.S. Balogh, K. Flórián, M. Matherny, Anal. Sci. 16 (2000) 973–974.
[42] I.S. Balogh, I.M. Maga, Á. Hargitai-Tóth, V. Andruch, Talanta 53 (2000) 543–549.
[43] V. Andruch, M. Telepčáková, I.S. Balogh, N. Urbanová, Microchim. Acta 142 (2003) 109–113.
[44] I.S. Balogh, V. Andruch, M. Kovács, Anal. Bioanal. Chem. 377 (2003) 709–714.
[45] I.S. Balogh, M. Ruschak, V. Andruch, Y. Bazel’, Talanta 76 (2008) 111–115.
[46] J. Škrlíková, V. Andruch, I.S. Balogh, L. Kocúrová, Y. Bazel’, Microchem. J., doi:10.1016/j.microc.2011.03.008.
[47] M. Rezaee, Y. Yamini, M. Faraji, J. Chromatogr. A 1217 (2010) 2342–2357.
[48] J. Aznarez, A. Ferrer, J.M. Rabadan, L. Marco, Talanta 32 (1985) 1156–1158.
[49] M.A. Wimmer, H.E. Goldbach, J. Plant Nutr. Soil Sci. 162 (1999) 15–18.
[50] P.S. Ramanjaneyulu, Y.S. Sayi, K.L. Ramakumar, J. Nucl. Mater. 378 (2008) 139–143.
[51] P.S. Ramanjaneyulu, Y.S. Sayi, K.L. Ramakumar, Indian J. Chem. Technol. 17 (2010) 468–470.
[52] CSN ISO 9390, Water Quality – Determination of borate, Spectrophotometric determination with azomethine-H, Czech normalization institute, 1996 (in Czech).