

This article was downloaded by: [Northwest Plateau Institute of Biology]

On: 27 March 2014, At: 20:03

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Analytical Letters

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lanl20>

### Determination of Boron Using Headspace Liquid Phase Micro-Sublimation Coupled with Inductively Coupled Plasma Optical Emission Spectrometry

Aide Sun<sup>a</sup>, Qingcai Xu<sup>a</sup>, Shujian Xu<sup>a</sup>, Xuehui Shangguan<sup>a</sup>, Hongyuan Shen<sup>a</sup> & Jing Sun<sup>b</sup>

<sup>a</sup> Shandong Provincial Key Laboratory of Soil Conservation and Environmental Protection, College of Resource and Environment, Linyi University, Linyi, China

<sup>b</sup> Key Laboratory of Adaptation and Evolution of Plateau Biota and Qinghai Key Laboratory of Qinghai-Tibet Plateau Biological Resources, Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining, China

Accepted author version posted online: 24 Jun 2013. Published online: 01 Oct 2013.

To cite this article: Aide Sun, Qingcai Xu, Shujian Xu, Xuehui Shangguan, Hongyuan Shen & Jing Sun (2013) Determination of Boron Using Headspace Liquid Phase Micro-Sublimation Coupled with Inductively Coupled Plasma Optical Emission Spectrometry, *Analytical Letters*, 46:16, 2610-2619, DOI: [10.1080/00032719.2013.803250](https://doi.org/10.1080/00032719.2013.803250)

To link to this article: <http://dx.doi.org/10.1080/00032719.2013.803250>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Atomic Spectroscopy

### DETERMINATION OF BORON USING HEADSPACE LIQUID PHASE MICRO-SUBLIMATION COUPLED WITH INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

Aide Sun,<sup>1</sup> Qingcai Xu,<sup>1</sup> Shujian Xu,<sup>1</sup> Xuehui Shangguan,<sup>1</sup> Hongyuan Shen,<sup>1</sup> and Jing Sun<sup>2</sup>

<sup>1</sup>Shandong Provincial Key Laboratory of Soil Conservation and Environmental Protection, College of Resource and Environment, Linyi University, Linyi, China

<sup>2</sup>Key Laboratory of Adaptation and Evolution of Plateau Biota and Qinghai Key Laboratory of Qinghai-Tibet Plateau Biological Resources, Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining, China

*Trace boron in water and plant samples was preconcentrated by a novel headspace liquid phase micro-sublimation method, followed by determination by inductively coupled plasma optical emission spectroscopy. Sodium hydroxide solution was used as the absorption solvent during the preconcentration step. The type and volume of absorption solvent, absorption time and temperature, and pH of the absorption solution and sample solution were optimized for the extraction. The linear range was from 0.1 to 80 µg/L, with a relative standard deviation of 7.4%. The limit of detection based on a signal-to-noise ratio of three was 0.008 µg/L. Under the optimized conditions, real water samples and plant samples were analyzed. The results showed this method can be applied for the determination of boron in environmental samples.*

**Keywords:** Boron; Determination; Headspace liquid phase micro-sublimation; Inductively coupled plasma optical emission spectrometry; Water

## INTRODUCTION

Boron is a significant micronutrient in biological systems, where it plays an essential role in embryonic development and organogenesis of plants and animals (Huang et al. 2005). To better understand the behavior of boron, its uptake,

Received 22 March 2013; accepted 30 April 2013.

This study was supported by the Program for Natural Science Foundation of China (Grant Nos. 41072138 and 41172160), the Program for Natural Science Foundation of Shandong Province, China (Grant No. ZR2010DM002), and the Knowledge Innovation Programs of the Chinese Academy of Sciences (No. KSCX2-EW-J-26).

Address correspondence to Jing Sun, Northwest Institute of Plateau Biology, Chinese Academy of Sciences, 23 Xinning Road, Xining 810008, China. E-mail: sunj@nwipb.cas.cn

translocation, and involvement in plant processes, the effects of boron deficiency and excess boron must be understood. The extraction of boron from environmental samples affects the application of analytical measurements, especially for the determination of its isotopic composition.

Boron has been extracted from environmental samples using traditional methods, such as ultraviolet irradiation, specific resins, activated carbon hydrogen peroxide (Muriel and Anne 1997), and bleaching methods with sodium hypochlorite combined with sodium hydroxide (Ni, Foster, and Elliott 2010; Vengosh et al. 1991; Hillaire-Marcel and De Vernal 2007). However, the organic matter remaining in the samples after these methods may affect the determination of boron isotopic composition by using thermal ionization mass spectrometry (Lemarchand et al. 2002). An effective method for the extraction and purification of boron was developed by Gaillardet et al. (2001) using the micro-sublimation of boron at low temperature. This method removes exogenous contaminants before isotopic analyses and has been successfully applied to river water samples (Chetelat et al. 2005; Lemarchand, Schott, and Gaillardet 2005). He et al. (2011) designed an effective and simple micro-sublimation apparatus suitable for laboratory use with capped 0.5 mL polyethylene centrifuge tubes that could hold 100  $\mu$ L of solution. The recovery for samples containing less than 50  $\mu$ g boron was 100%. In the procedure of micro-sublimation, the tube was heated in an oven at 70°C for 28 h. After the solution was evaporated to dryness, the boron sublimed into the gas phase at the top of the tubes. However, boron was absorbed on to the inner wall of the polyethylene tubes unless a water layer was included at the top of the tube, which increased the micro-sublimation time.

Headspace analysis of volatile organic compounds (VOC) in aqueous samples is well-known for the complete elimination of organic interferences from the sample matrix (Jeannot and Cantwell 1996; Theis et al. 2001; Zhao, Lao, and Xu 2004). The aim of the present study was to develop a method combining headspace and the micro-sublimation technique, and was named headspace liquid phase micro-sublimation (HS-LPMS) for the extraction of boron. Potential factors affecting the efficiency of HS-LPMS, including extraction time, temperature, type and volume of extraction solvent, headspace volume, and pH of absorption and sample were investigated. The validity of HS-LPMS was also tested by the analysis of several environmental samples.

## EXPERIMENTAL

### Reagents

Sodium hydroxide, hydrochloric acid, nitric acid and boric acid were guaranteed reagents. Amberlite 743 IRA resin was purchased from Sigma-Aldrich Shanghai Trading Co., Ltd. (Shanghai, China). Dowex 50 W  $\times$  8 cation resin (200–400 mesh) was purchased from J&K Scientific Ltd (Beijing, China). Before used, 0.5 mL polyethylene centrifuge tubes were soaked in hydrochloric acid solution overnight, washed with deionized water at least 10 times, and dried in an oven.

Stock and working standards were prepared with deionized water. To eliminate matrix effects, hydrochloric acid was evaporated in a sealed vessel, and deionized water was passed through the Amberlite 743 IRA resin column.

## Apparatus

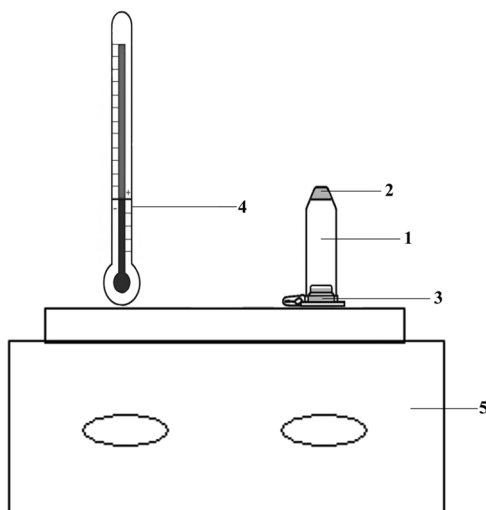
Inductively coupled plasma optical emission spectrometry (ICP-OES, Vista MPX, Varian, USA) with a 40 MHz RF generator and a charge coupled device detector (VistaChip) was used for the determination of boron. The spectrometer was operated in a transient signal acquisition mode. An axial-viewing quartz torch, a cyclonic spray chamber, a glass concentric nebulizer, and a peristaltic pump were used. The measurements were carried out using the manufacturer's default conditions with a RF generator power of 1.0 kW, plasma gas flow rate at 15.0 L/min, auxiliary gas flow rate at 1.5 L/min, nebulizer gas pressure at 200 kPa, replicate read time of 5 s, and a pump rate at 15 rpm.

## Headspace Liquid Phase Micro-Sublimation Procedure

A 0.5-mL conical tube with a lid containing 100  $\mu$ L of standard solution or sample solution (100  $\mu$ g B/mL) and 100  $\mu$ L of absorption solvent at the top was placed inverted on an electric hotplate at 70°C. After extraction for 10 h, the absorption solvent was analyzed for boron. A diagram of the HS-LPMS apparatus is shown in Figure 1.

## Pretreatment of Environmental Samples using HS-LPMS Combined with Ion Exchange

Boron in water and plant samples were extracted by ion exchange combined with HS-LPMS. Local river water, well water, tap water, and plant samples (leaves of *Flos Lonicerae* and flowers and stems of *Echinacea purpurea Moench*) were collected for the analysis. Water samples were passed through a 0.45- $\mu$ m polycarbonate membrane



**Figure 1.** Apparatus for the headspace liquid phase micro-sublimation of boron. 1) Centrifuge tube (0.5 mL); 2) Absorption solvent; 3) Sample solution; 4) Thermometer; 5) Automatic temperature-controlled heater.

before separation. Plant samples were washed repeatedly with deionized water to remove any matters adhered to the surface, and then dried in a stream of air at 50°C. The dried samples were powdered to 100–200 mesh. Plant samples were digested with nitric acid solution and then isolated from the solution by two chromatographic steps (Wang et al. 2002; Ma et al. 2011).

Boron was extracted using a modification of the method developed by Wang et al. (2002). The sample solution was loaded onto preconditioned Amberlite IRA 743 resin (100–120 mesh) at a flow rate of 2.5 mL/min. After rinsing with high-purity water, the resin was eluted with 10 mL of 0.1 mol/L HCl at 75°C. The eluate was then evaporated to about 0.5 mL at 60°C under a clean air stream. The condensed solution was quickly passed through a mixed ion-exchange resin column containing a strong acidic resin (200–400 mesh, Dowex 50 W × 8) and a weak alkaline anion resin (60–100 mesh). The column was eluted with 10 mL of high-purity water, and the eluate was collected in a Teflon beaker. After evaporation to about 0.5 mL at 60°C under a clean air stream, the sample was transferred to a 0.5-mL centrifuge tube and evaporated to approximately 0.1 mL (Ma et al. 2011). Boron in the solution was then extracted using HS-LPMS for 10 h under the optimum conditions. The amount of boron in the extraction solvent was determined by ICP-OES.

## RESULTS AND DISCUSSION

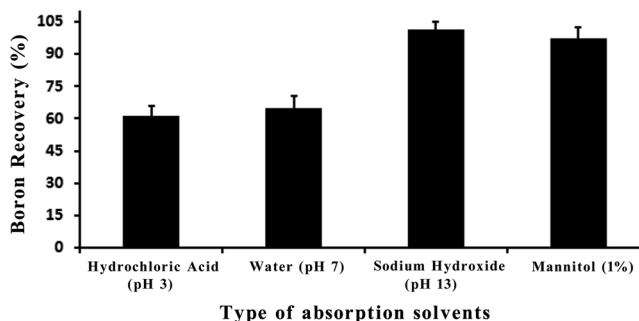
HS-LPMS was applied for the extraction of boron from an aqueous solution into headspace. To optimize the method, the type and volume of absorption solvent, temperature, absorption time, and pH in absorption solvent and sample solution were investigated. The recovery of boron in the extraction solvent was calculated using the following equation:

$$R = m_e/m_0 \quad (1)$$

where  $R$ ,  $m_e$ , and  $m_0$  are the recovery of boron by HS-LPMS, amount of boron in the absorption solvent, and initial amount of the boron in the aqueous sample in the lid of the conical tube, respectively.

### Preliminary Selection of the Absorption Solvent

The selection of an appropriate absorption solvent is essential for HS-LPMS, which is influenced by the chemical nature of boron. A solvent with good boron-absorption ability should be used for analysis. Aqueous solutions with different pH values were tested for boron absorption in the headspace. The hydrochloric acid solution, water, sodium hydroxide solution and mannitol solution (1%) were considered. The absorption solvents (100  $\mu$ L) were tested for extracting boron from aqueous samples containing boron of 10  $\mu$ g B/mL at 70°C for 10 h. The sodium hydroxide solution gave the best extraction efficiency (Figure 2). The efficiency of mannitol solution (1%) was found to be close to that of sodium hydroxide solution. The enrichment of H<sup>+</sup> ions in the low pH solution (hydrochloric acid solution) might prevent boron from being absorbed from the headspace into the absorption solvent. By comparison, in the high pH solution (sodium hydroxide solution), reaction



**Figure 2.** Effect of the type of absorption solvent on boron recovery. Extraction conditions: 0.1 mL sample, 100  $\mu$ L absorption solvent, sample pH of 5.0, 10 h absorption time, temperature at 70°C.

between boric acid and sodium hydroxide could accelerate the absorption of boron from the headspace. Therefore, in subsequent experiments, sodium hydroxide solution was chosen as the absorption solvent.

### Effect of the Volume of the Absorption Solvent and Headspace

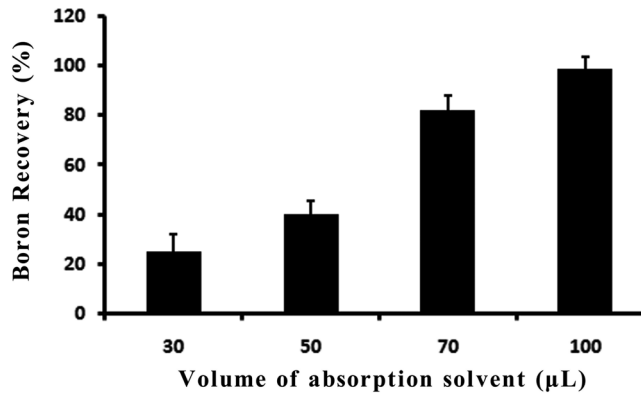
In headspace liquid phase microextraction (HS-LPME), the equilibrium process is dependent on the absorption time (De Jager and Andrews 1999), whereas, in HS-LPMS, the absorption efficiency is dependent on the exhaustive extraction rather than absorption time. The following equation describes the amount of analyte concentrated by the extraction solvent in a micro-drop (Przyjazny and Kokosa 2002):

$$n = \frac{K_{ODW} V_D C_0 V_S}{K_{ODW} V_D + K_{GW} V_H + V_S} \quad (2)$$

This can be transformed to the following equation:

$$\frac{1}{n} = \frac{1}{C_0} \left[ \frac{1}{V_S} + \frac{1}{K_{ODW} V_D} + \left( \frac{K_{GW} V_H}{V_S} + 1 \right) \right] \quad (3)$$

where  $n$  is the amount of the analyte absorbed by the absorption solvent when partition equilibrium is attained;  $K_{ODW}$  and  $K_{GW}$  are the absorption solvent-water (sample) and the gas-water distribution coefficients, respectively;  $C_0$  is the initial concentration of analyte in the matrix;  $V_D$ ,  $V_S$ , and  $V_H$  are the volumes of the absorption solvent, sample, and headspace, respectively. From Equation (3), it can be seen that the volume of absorption solvent and the volume of headspace could affect the HS-LPMS efficiency. Equation (3) shows that as  $V_S$  and  $V_D$  increase,  $n$  also increases. Furthermore, as  $V_H$  decreases,  $n$  increases. To increase the efficiency of HS-LPMS, the volume of the sodium hydroxide solution was optimized. With a fixed volume of the tube, the absorbent volume was directly related to the headspace volume. The ratio between the headspace volume and the volume of absorption solvent was optimized in experiments using 0.5 mL vials. The volume of sodium hydroxide solution was increased from 30 to 100  $\mu$ L for extraction of



**Figure 3.** Effect of the volume of absorption solvent on the recovery of boron. Extraction conditions: 0.1 mL sample, sample pH of 5.0, absorbent pH of 13, absorption time of 10 h, temperature at 70°C.

boron. As shown in Figure 3, the recovery rate of boron increased as the volume of sodium hydroxide solution increased and the headspace volume decreased.

The aqueous mass-transfer coefficient  $\beta_{aq}$ , based on the penetration theory of mass transfer of solute can be described as follows:

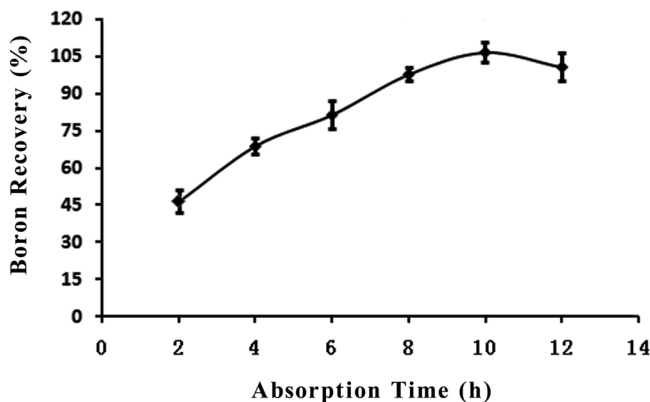
$$\beta_{aq} = 2 \left( \frac{D_{aq}}{\pi t_e} \right)^{1/2}, \quad (4)$$

where  $D_{aq}$  is the diffusion coefficient in the aqueous phase and  $t_e$  is the exposure time of a small fluid volume element of one phase momentarily in contact with another phase (Zhao et al. 2004). According to this theory, as the volume of the absorption solvent increases, the exposure interface between the headspace and absorption solvent solution increases,  $\beta_{aq}$  increases, and  $t_e$  decreases. When an absorbent volume of 100  $\mu\text{L}$  was used, 100% recovery of boron was obtained. Using a larger volume of absorption solvent (>100  $\mu\text{L}$ ) can increase the efficiency of HS-LPMS; however, when the volume is above 120  $\mu\text{L}$ , the absorption solution at the top is easy to drop. Therefore, in subsequent experiments, a volume of 100  $\mu\text{L}$  was used.

### Effect of Extraction Time

The amount of boron absorbed at a given duration depends on the mass transfer of boron from the aqueous sample to the absorption solution. This process requires some time to reach equilibrium. The absorption time was optimized by monitoring the recovery for extraction of a 100- $\mu\text{L}$  boron working solution at 70°C. As the extraction time increased to 10 h, the recovery of boron increased to 100% (Figure 4). When the extraction time was above 10 h, the recovery remained constant. Therefore, in all subsequent experiments, 10 h was employed. In comparison with the micro-sublimation time (28 h) reported by Lemarchand et al. (2002) and He et al. (2011), the absorption time in the present study was much shorter.

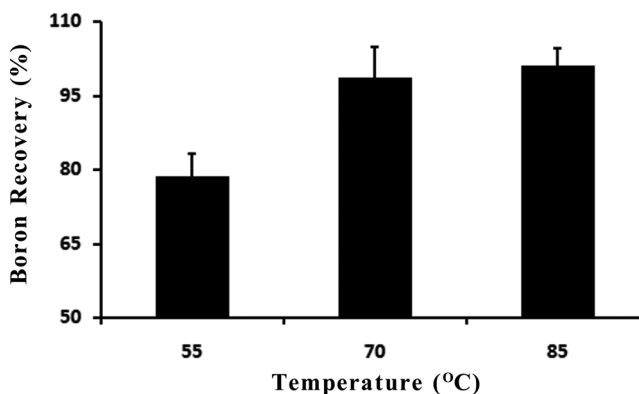




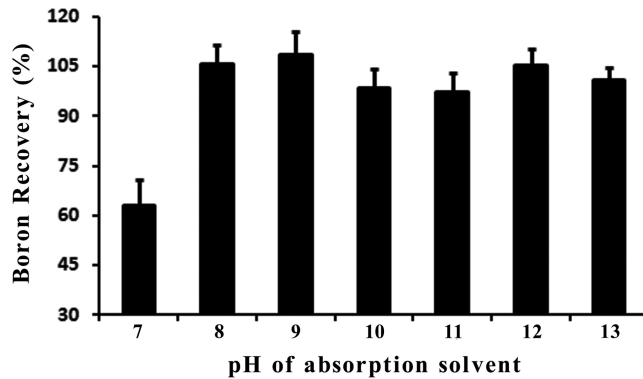
**Figure 4.** Effect of the absorption time on the recovery of boron. Extraction conditions: 0.1 mL sample, 100  $\mu$ L absorption solvent, sample pH of 5.0, absorbent pH of 13, temperature at 70°C.

### Effect of Absorption Temperature

Temperature is an important factor that affects both the absorption efficiency and the solubility. At high temperatures, diffusion coefficients in aqueous solution are high and the extraction time is short, and the solubility is also high. Both of these two effects were taken into consideration during the optimization experiments. Temperatures of 55°C, 70°C, and 85°C were investigated. The absorption efficiency of boron increased with temperature being increased from 55–85°C (Fig. 5). Initially, the recovery increased with the temperature. When the temperature exceeded 70°C, the increase in boron recovery gradually leveled off. Presumably, before equilibrium was reached, the concentration of boron in the aqueous solution was greater than that in the headspace, and the analyte molecules diffused from the aqueous solution to the gas phase, which is dependent on the diffusion velocity. In subsequent experiments, 70°C was used for the extraction, which is consistent with the temperature used by He et al. (2011).



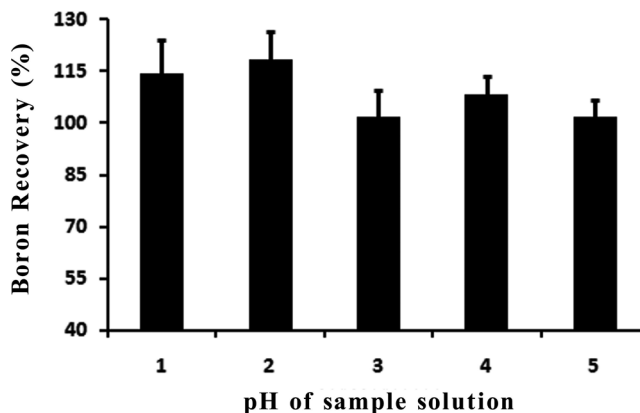
**Figure 5.** Effect of the temperature on the recovery of boron. Extraction conditions: 0.1 mL sample, 100  $\mu$ L absorption solvent, sample pH of 5.0, absorbent pH of 13, absorption time of 10 h.



**Figure 6.** Effect of the pH of absorption solvent on the recovery of boron. Extraction conditions: 0.1 mL sample, 100  $\mu$ L absorption solvent, sample pH of 5.0, absorption time of 10 h, temperature at 70°C.

### Effect of pH

The pH is an important factor for quantitative recovery of boron because boron compound formation depends on the pH of the aqueous solution. In this study, pH values of 7 to 13 for the sodium hydroxide solution and 1 to 5 for the sample solution were investigated. The pH was adjusted using hydrochloric acid or sodium hydroxide solution. The results for the sodium hydroxide solution experiments are shown in Figure 6 and those for the sample solutions shown in Figure 7. When the pH was between 8 and 13, the recovery of boron from the aqueous samples was around 100% (Fig. 6). However, the reproducibility for the recoveries at high pH (13) was much better than that at low pH (8–10). A likely explanation is that the amount of hydroxyl ion in the absorption solvent could affect the extraction efficiency of boron. After the solution was dried, and boron evaporated into gas phase, the gaseous boron reacted with hydroxide ions in solution. However, when the hydroxide ion supply was exhausted, boron in gas phase dissolved in the



**Figure 7.** Effect of the pH of sample on the recovery of boron. Extraction conditions: 0.1 mL sample, 100  $\mu$ L absorption solvent, absorbent pH of 13, absorption time of 10 h, temperature at 70°C.

**Table 1.** Boron results for environmental samples by HS-LPMS

Sample	Concentration	Added amount ( $\mu\text{g}$ )	Recoveries (%)
Tap water	12.3 ( $\mu\text{g/L}$ )	0.3	98.7
River water	69.4 ( $\mu\text{g/L}$ )	0.3	100.2
Underground water	127.4 ( $\mu\text{g/L}$ )	0.3	103.3
Leaves of <i>Flos Lonicerae</i>	22.0 ( $\mu\text{g/g}$ )	0.3	99.6
Flowers of <i>Echinacea purpurea Moench</i>	17.1 ( $\mu\text{g/g}$ )	0.3	105.8
Stems of <i>Echinacea purpurea Moench</i>	23.2 ( $\mu\text{g/g}$ )	0.3	102.2

absorption solvent, which decreased the velocity of the absorption. Consequently, a sodium hydroxide solution at pH 13 was chosen for the subsequent experiments.

Figure 7 shows that the pH ranging from 1 to 5 of the sample solution also affected the extraction efficiency of boron using HS-LPMS. The recovery of boron could reach 100% as the pH changed. The recovery of boron was almost 120% for the pH 2 sample and 115% for the pH 1 sample. This indicates that perhaps there is a substantial blank contribution to the determination of boron at low pHs of sample solution. Although the addition of hydrochloric acid facilitates boron evaporation, the absorbent in the headspace could react with hydrochloric acid, which affects the absorption efficiency of boron in gas phase. The trials on the solution with pH more than 7 showed that there was not any boron determined in the absorption solvent. A sample solution of pH 5 was selected for subsequent experiments.

### Analytical Performance

Under the optimum experimental conditions, the linear range (0.1–80  $\mu\text{g/mL}$ ) and coefficient of determination ( $R^2 = 0.9982$ ) were determined. The reproducibility was investigated in five replicate experiments under the optimized conditions using an aqueous standard solution of 10  $\mu\text{g B/mL}$ . The relative standard deviation was 7.4%. The limit of detection based on a signal-to-noise ratio of three was 0.008  $\mu\text{g/mL}$ .

### Analysis of Environmental Samples

Authentic environmental samples, including water and plant samples, were used to assess the applicability of the proposed method. The experimental results (Table 1) indicated that the recoveries of boron in the water samples were quantitative. The concentrations of boron ranged from 12.3 to 127.4  $\mu\text{g/L}$  in the water samples, and from 17.1 to 23.2  $\mu\text{g/g}$  in the plant samples. The recovery range in the six samples was 98.7–105.8%, which demonstrates that the water and plant sample matrices have little effect on the HS-LPMS.

### CONCLUSIONS

An extraction method was optimized for the determination of boron by HS-LPMS from water and plant samples. The type and volume of absorption solvent, absorption time, temperature, and pH of the absorption solvent and samples

were investigated. The linear range of the method suggests that this method can be successfully applied for the determination of boron in environmental samples.

## REFERENCES

- Chetelat, B., J. Gaillardet, R. Freydier, and P. Négrel. 2005. Boron isotopes in precipitation: Experimental constraints and field evidence from French Guiana. *Earth Planet Sci. Lett.* 235: 16–30.
- De Jager, L. S., and A. R. J. Andrews. 1999. Solvent microextraction of chlorinated pesticides. *Chromatographia*. 50: 733–738.
- Gaillardet, J., D. Lemarchand, C. Göpel, and G. Manhès. 2001. Evaporation and sublimation of boric acid: Application for boron purification from organic rich solutions. *Geostand. Newslett.* 25: 67–75.
- Grottoli, A. G., L. J. Rodrigues, K. A. Matthews, J. E. Palardy, and O. Gibb. 2005. Pre-treatment effects on coral skeletal  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . *Chem. Geol.* 221: 225–242.
- He, M. Y., Y. K. Xiao, Y. Q. Ma, Z. D. Jin, and J. Xiao. 2011. Effective elimination of organic matter interference in boron isotopic analysis by thermal ionization mass spectrometry of coral/foraminifera: micro-sublimation technology combined with ion exchange. *Rapid Commun. Mass Spectrom.* 25: 743–749.
- Hillaire-Marcel, C., and A. De Vernal. 2007. *Proxies in Late Cenozoic Paleoceanography*. Montreal, Canada: Elsevier.
- Huang, L., Z. Ye, R. W. Bell, and B. Dell. 2005. Boron nutrition and chilling tolerance of warm climate crop species. *Ann. Bot.* 96: 755–767.
- Jeannot, M. A., and F. F. Cantwell. 1996. Solvent microextraction into a single drop. *Anal. Chem.* 68: 2236–2240.
- Lemarchand, D., J. Gaillardet, C. Göpel, and G. Manhès. 2002. An optimized procedure for boron separation and mass spectrometry analysis for river samples. *Chem. Geol.* 182: 323–334.
- Lemarchand, D., J. Schott, and J. Gaillardet. 2005. Boron isotopic fractionation related to boron sorption on humic acid and the structure of surface complexes formed. *Geochim. Cosmochim. Acta* 69: 3519–3533.
- Ma, Y. Q., Y. K. Xiao, M. Y. He, J. Xiao, Q. Shen, and S. X. Jiang. 2011. Boron isotopic composition of Paleozoic brachiopod and coeval coral calcites in Yunnan-Guizhou Plateau. *China. Sci. Chin. Earth Sci.* 41: 984–999.
- Muriel, B., and J. L. Anne. 1997.  $\text{H}_2\text{O}_2$  treatment of recent coral aragonite: oxygen and carbon isotopic implications. *Chem. Geol.* 143: 171–180.
- Ni, Y. Y., G. L. Foster, and T. Elliott. 2010. The accuracy of  $\delta^{11}\text{B}$  measurements of foraminifers. *Chem. Geol.* 274: 187–195.
- Przyjazny, A., and J. M. Kokosa. 2002. Analytical characteristics of the determination of benzene, toluene, ethylbenzene and xylenes in water by headspace solvent microextraction. *J. Chromatogr. A*. 977: 143–153.
- Theis, A. L., A. J. Waldack, S. M. Hansen, and M. A. Jeannot. 2001. Headspace solvent microextraction. *Anal. Chem.* 73: 5651–5654.
- Vengosh, A., K. Yehoshua, S. Abraham, R. C. Allan, and M. Malcolm. 1991. Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochim. Cosmochim. Acta*. 55: 2901–2910.
- Wang, Q. Z., Y. K. Xiao, Y. H. Wang, C. G. Zhang, and H. Z. Wei. 2002. Boron separation by the two-step ion-exchange for the isotopic measurement of boron. *Chin. J. Chem.* 20: 45–50.
- Zhao, R. S., W. J. Lao, and X. B. Xu. 2004. Headspace liquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination. *Talanta*. 62: 751–756.