



Trace Determination of Tetrabromobisphenol A in Water Samples with Temperature Controlled Ionic Liquid Dispersive Microextraction

J.P. YUAN^{1,*}, J.H. LIU², S.S. WANG² and Z.J. CUI^{1,*}

¹School of Environmental Science and Engineering, Shandong University, Jinan 250100, P.R. China

²Key Laboratory for Applied Technology of Sophisticated Analytical Instruments of Shandong Province, Analysis and Test Center, Shandong Academy of Sciences, Jinan 250014, P.R. China

*Corresponding authors: E-mail : yuanjip@126.com; cuizj@sdu.edu.cn

(Received: 30 June 2011;

Accepted: 8 February 2012)

AJC-11054

A sensitive method based on temperature controlled ionic liquid dispersive microextraction combined with high performance liquid chromatography-electrospray tandem mass spectrometry (HPLC-ESI-MS-MS) has been developed for the determination of trace tetrabromobisphenol A in water samples. In temperature controlled ionic liquid dispersive microextraction, toxic organic solvents for extraction and dispersion were free. Some important factors that may influence the extraction recovery were investigated and optimized. Under the optimum conditions, excellent linearity was obtained in the range of 0.5-50 $\mu\text{g L}^{-1}$ with correlative coefficient (R) 0.9987. The limit of detection was 0.05 $\mu\text{g L}^{-1}$ and the relative standard deviation (RSD) was 7.70 % (n = 6). The proposed method was successfully applied to analyze real environmental water samples. The satisfactory spiked recoveries were in the range of 92.4-103.9 % and relative standard deviations were in the range of 3.31-8.68 %.

Key Words: Tetrabromobisphenol A, Temperature controlled ionic liquid dispersive microextraction, Water samples.

INTRODUCTION

Tetrabromobisphenol A (TBBPA), an additive or reactive brominated flame retardant (BFR), is used extensively in electronic equipments and polymers. Its market size of global consumption increased to 170,000 tons in 2004 and the production in China reached to 18,000 tons/yr in 2006^{1,2}. Because it can act as thyroid hormone, estrogen agonist and show the toxicity to aquatic life^{3,4}, the fate and distribution of this contaminant are of high concern. Many studies have reported its occurrence in various environmental matrices, even in wildlife and human serum. From the official journal of the European union, the evaluation and testing of tetrabromobisphenol A for the aquatic ecosystem are needed to precede¹. Therefore, simple and sensitive method is needed for the determination of trace tetrabromobisphenol A in environmental aquatic samples for safety evaluation.

The most widely used methods for tetrabromobisphenol A determination are carried out with necessary pretreatments prior to chromatographic techniques, including gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). After the comparison of above chromatographic techniques, HPLC-MS/MS was considered as a method of choice, not only because of its higher sensitivity and better detection limits, but also

because derivatization is not needed⁵. Whereas, derivatization is required before GC-MS analysis and has been reported to produce errors and analyte losses¹.

Regarding sample pretreatments, conventional sample pretreatments (e.g. liquid-liquid extraction and Soxhlet extraction) are time-consuming, tedious and often need a large amount of toxic solvent. Microextraction technique could overcome these demerits and was a typical example of simplification and miniaturization trends⁶. This method has been applied for the enrichment and determination of many pollutants in environmental water samples⁷⁻¹⁰. However, the extractant and disperser solvent, such as carbon tetrachloride, methanol, chlorobenzene or chloroform, were typically toxic¹¹. Zhou *et al.*¹² has developed a novel and environmental benign method, termed temperature controlled ionic liquid dispersive microextraction (TCILDME), which has been successfully used to analyze the triclosan and triclocarban, DDT and its metabolites, hexabromocyclododecane and anthraquinones in environmental and Chinese medicine samples¹¹⁻¹⁵. This method was based on the increasing temperature making ionic liquid (IL) completely disperse in the aqueous phase and increase the chance of mass transfer into ionic liquid phase and the ionic liquid was deposited into one drop by cooling and centrifugation¹². To the best of our knowledge, temperature

controlled ionic liquid dispersive microextraction has not been applied for the analysis of tetrabromobisphenol A in water samples. In the present study, temperature controlled ionic liquid dispersive microextraction combined with HPLC-ESI-MS/MS was developed to determine the tetrabromobisphenol A at trace level in water samples. Influence factors of extraction efficiency were studied and optimized. The proposed method was successfully used for the analysis of tetrabromobisphenol A in real water samples.

EXPERIMENTAL

Both methanol and ammonium acetate of HPLC grade were obtained from Tedia Company Inc. (Fairfield, Ohio, USA). 1-Butyl-3-methylimidazolium hexafluorophosphate [C₄MIM][PF₆] (99 % purity), 1-hexyl-3-methylimidazolium hexafluorophosphate [C₆MIM][PF₆] (99 %) and 1-octyl-3-methylimidazolium hexafluorophosphate [C₈MIM][PF₆] (99 %) were all purchased from Chengjie chemical company (Shanghai, China). Technical tetrabromobisphenol A with a concentration of 100 µg/mL (99 % purity) was obtained from Accustandards (New Haven, CT).

An Agilent 1200 HPLC equipped with 1200 Binary SL pump and 6410 triple quadrupole mass spectrometry (Palo Alto, CA, USA) was employed for the analysis. Separation was performed with an Eclipse XDB-C₁₈ column (2.1 mm × 100 mm, 1.8 µm particle size) at 30 °C. The flow rate of the mobile phase consisting of 85 % methanol and 15 % water with 0.1 % ammonium acetate was at 0.5 mL min⁻¹ in constant. Quantification of tetrabromobisphenol A was achieved in multiple reaction monitoring mode (MRM) after optimization.

Temperature controlled ionic liquid dispersive microextraction procedure: For the temperature controlled ionic liquid dispersive microextraction procedure, a 10 mL screw cap glass conical tube containing 70 µL [C₆MIM][PF₆] and 5 mL aqueous solution spiked with 10 µg L⁻¹ tetrabromobisphenol A, was heated in the water bath at 60 °C. Ionic liquid dispersed into infinite droplets and the solution was gradually clarified. Thereafter, the tube was stored at 0 °C for 15 min and centrifuged for 5 min at 3000 rpm. Meanwhile, ionic liquid was separated and deposited in the bottom of the conical tube. Finally, the upper aqueous phase was removed with the syringe and settled phase was diluted with methanol of 70 µL. And 10 µL was injected with autosampler into HPLC-ESI-MS/MS.

RESULTS AND DISCUSSION

In this microextraction procedure, many factors that might influence extraction recovery, such as type and volume of ionic liquid, dispersive temperature, sample pH, extraction time and concentration of salt, were investigated and optimized in detail.

The results of trial experiments of temperature controlled ionic liquid dispersive microextraction from different type extractant indicated that [C₆MIM][PF₆] was the best choice amongst [C₄MIM][BF₄], [C₆MIM][PF₆] and [C₈MIM][PF₆]. Therefore, [C₆MIM][PF₆] was chosen as extractant in the further experiments. Ionic liquid volume was an important influence factor in microextraction procedure. Too little or

excessive ionic liquid would result in the difficult separation from the aqueous solution and/or less sensitivity (high LOD). In this study, experiments with ionic liquid volume from 50 µL to 90 µL were performed to investigate the effect of recovery under the same conditions. As shown in the results, the peak area of tetrabromobisphenol A increased with the increase of ionic liquid volume between 50 and 70 µL and then decreased gradually with the increase of ionic liquid volume. Thus, 70 µL [C₆MIM][PF₆] was adopted in the following study. The depressive temperature was a significant parameter in temperature controlled ionic liquid dispersive microextraction. Higher temperature could quickly drive ionic liquid to disperse completely into the aqueous solution and increase the mass transfer between ionic liquid and aqueous solution. From the results of a series of experiments performed in the range of 50-80 °C, excellent extraction efficiency was obtained at 60 °C and then remained constant with the increase of temperature. Therefore, the dispersive temperature was fixed at 60 °C in the subsequent experiments.

Tetrabromobisphenol A could ionize in alkalescence circumstance and exit as molecule in acid medium due to containing two hydroxyl radicals in its structure. The effect of sample pH was evaluated in the range of 2-10 by adding hydrochloric acid or ammonia to aqueous solution. The results showed that the recovery of tetrabromobisphenol A increased with the increase of pH value and the maximum peak area of tetrabromobisphenol A was at pH 4. Then the recovery decreased significantly with the continuous increase of pH value. Based on these results, pH 4 of sample solution was selected in the further experiments.

Mass transfer in dispersive liquid phase microextraction was a time-cost procedure, which needs appropriate extraction time to transfer the target compounds from water into extractant till reaching the balance. In this study, the extraction time is defined as the time interval of the conical tube in thermostatic water. In order to obtain the best performance, the extraction time was optimized over the range of 5-25 min with already optimal conditions. It can be concluded that the recovery increased between 5 and 15 min and then reached a constant value. To save the experimental time, 15 min was the best choice in the study.

The effect of salt concentration was assessed in range of 0-10 % (w/v) by adding sodium chloride. The results indicated that the recovery of tetrabromobisphenol A kept almost constant in the range of 0-6 % of NaCl concentration and decreased significantly as more than 6 %. It could be attributed to the fact that the excessive salt enhanced the ion exchange between [PF₆⁻] in [C₆MIM][PF₆] and Cl⁻ in solution and the resulting [C₆MIM]Cl is soluble in water¹⁶.

Under the above optimum conditions, linearity was observed over the range of 0.5-50 µg L⁻¹ with the coefficient of correlation (R) 0.9987. The limits of detection (LOD), based on a signal-to-noise ratio (S/N) of 3, was 0.05 µg L⁻¹. The relative standard deviation was 7.70 % (n = 6). Compared with previous DLPME-HPLC-MS/MS¹³ and SPE-HPLC-MS/MS¹⁷ methods, the features of the proposed method are comparable. However, the toxic extraction and disperser solvent were free in comparison with other methods.

In order to evaluate the proposed method, three real environmental water samples were analyzed. Tap water samples were analyzed directly. Yellow river and snow water samples were filtered through 0.45 micropore membrane prior to analysis. The results shown in Table-1 indicated that tetrabromobisphenol A could not be found in all samples. The satisfactory spiked recovery was obtained in the range of 92.4-103.9 % at the spiked concentration of 0.5 and 5.0 $\mu\text{g L}^{-1}$ and no matrix effect occurred in temperature controlled ionic liquid dispersive microextraction. The chromatograms of typical water samples and spiked samples are shown in Fig. 1.

TABLE-1
EXPERIMENTAL RECOVERIES OF
TETRABROMOBISPHENOL-A FROM
THREE SPIKED REAL WATER SAMPLES

Water samples	Found	Spiked ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)
Tap water	NDa	0.5	93.7	6.94
		5.0	103.9	6.64
River water	ND	0.5	101.1	8.11
		5.0	102.5	8.68
Snow water	ND	0.5	92.4	3.31
		5.0	98.2	8.64

a: Not detected

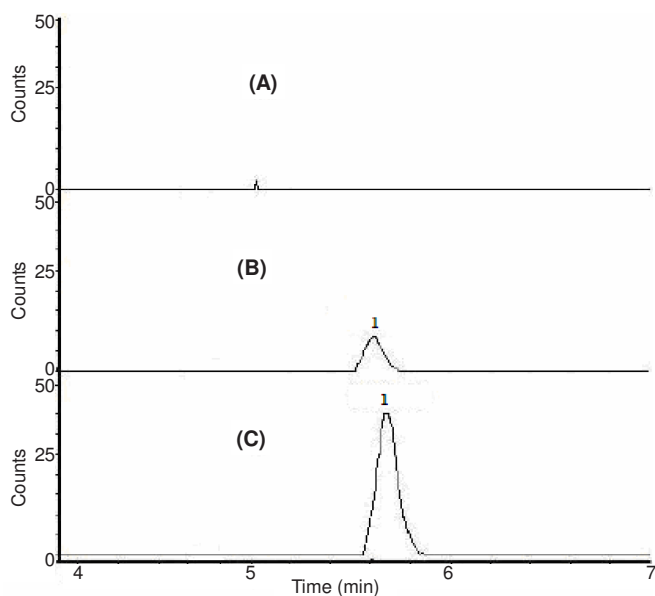


Fig. 1. Typical HPLC-ESI-MS/MS chromatograms of water samples. (A) River water sample; (B) River water sample spiked with 0.5 $\mu\text{g L}^{-1}$ tetrabromobisphenol A; (C) River water sample spiked with 5.0 $\mu\text{g L}^{-1}$ tetrabromobisphenol A. (1) tetrabromobisphenol A

Conclusion

In the proposed temperature controlled ionic liquid dispersive microextraction method, the low LOD and satisfactory spiked recovery of tetrabromobisphenol A were obtained from the real environmental water samples demonstrated the advantages of simplicity, sensitivity and environmental benign. It can be concluded that the developed method would be useful and suitable for the routine analysis of tetrabromobisphenol A in environmental water samples.

ACKNOWLEDGEMENTS

This work is financially supported by National Natural Science Foundation of China (21007035), the Scientific and Technological Developing Project of Shandong Province (No. 2011SJGZ03), Natural Science Foundation of Shandong Province (ZR2010BL029) and Basic Foundation of Shandong Academy of Sciences and Analysis and Test Center of Shandong province.

REFERENCES

1. A. Covaci, S. Voorspoels, M.A.-E. Abdallah, T. Geens, S. Harrad and R.J. Law, *J. Chromatogr. A*, **1216**, 346 (2009).
2. X.-L. Zhang, X.-J. Luo, S.-J. Chen, J.-P. Wu and B.-X. Mai, *Environ. Pollut.*, **157**, 1917 (2009).
3. M. Ghisari and E.C. Bonefeld-Jorgensen, *Mol. Cell. Endocrinol.*, **244**, 31 (2005).
4. M.H.A. Kester, S. Bulduk, H. van Toor, D. Tibboel, W. Meini, H. Glatt, C.N. Falany, M.W. H. Coughtrie, A.G. Schuur, A. Brouwer and T.J. Visser, *J. Clin. Endocrinol. Metab.*, **87**, 1142 (2002).
5. M. Frederiksen, K. Vorkamp, R. Bossi, F. Rigét, M. Dam and B. Svensmark, *Int. J. Environ. Anal. Chem.*, **87**, 1095 (2007).
6. M. Rezaee, Y. Assadi, M.-R.M. Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, *J. Chromatogr. A*, **1116**, 1 (2006).
7. H. Farahani, P. Norouzi, R. Dinarvand and M.R. Ganjali, *J. Chromatogr. A*, **1172**, 105 (2007).
8. N. Fattahi, Y. Assadi, M.R.M. Hosseini and E.Z. Jahromi, *J. Chromatogr. A*, **1157**, 23 (2007).
9. Y. Liu, E. Zhao, W. Zhu, H. Gao and Z. Zhou, *J. Chromatogr. A*, **1216**, 885 (2009).
10. E.Z. Jahromi, A. Bidari, Y. Assadi, M.R.M. Hosseini and M.R. Jamali, *Anal. Chim. Acta*, **585**, 305 (2007).
11. R.S. Zhao, X. Wang, J.P. Yuan, S.S. Wang and C.G. Cheng, *Chin. Chem. Lett.*, **22**, 97 (2011).
12. Q. Zhou, H. Bai, G. Xie and J. Xiao, *J. Chromatogr. A*, **1177**, 43 (2008).
13. R.-S. Zhao, X. Wang, J. Sun, J.-P. Yuan, S.-S. Wang and X.-K. Wang, *J. Sep. Sci.*, **33**, 1842 (2010).
14. H. Bai, Q. Zhou, G. Xie and J. Xiao, *Anal. Chim. Acta*, **651**, 64 (2009).
15. H.-F. Zhang and Y.-P. Shi, *Talanta*, **82**, 1010 (2010).
16. S. Gao, J. You, X. Zheng, Y. Wang, R. Ren, R. Zhang, Y. Bai and H. Zhang, *Talanta*, **82**, 1371 (2010).
17. R.-S. Zhao, X. Wang and J.-P. Yuan, *J. Sep. Sci.*, **33**, 1652 (2010).