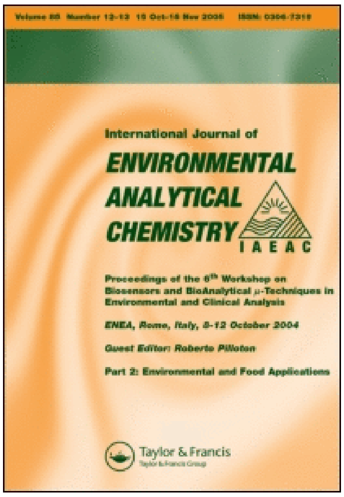

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1-Butyl-3-methylimidazolium hexafluorophosphate ionic liquid-based liquid–liquid microextraction for the determination of 4-nonylphenol and 4-*tert*-octylphenol in environmental waters

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In the present study, room-temperature ionic liquid (RTIL) 1-butyl-3-methylimidazolium hexafluorophosphate was used as extraction solvent in a liquid–liquid microextraction (LLME) procedure followed by liquid chromatography for determining 4-nonylphenol (4-NP) and 4-*tert*-octylphenol (4-*t*-OP) in environmental water samples. RTIL-based LLME was a simple, inexpensive, and fast sample preparation method, and its parameters such as extraction time, addition of salt, selection of phase ratio, and pH value were optimized. The optimized method had acceptable limits of detection (LOD) and a precision of $2\,\mu g\,L^{-1}$ and 8.1% for 4-NP and $0.6\,\mu g\,L^{-1}$ and 3.7% for 4-*t*-OP, respectively. The proposed method was successfully applied in river water and effluent from a sewage-treatment plant, and the recoveries spiked at $6\,\mu g\,L^{-1}$ and $25\,\mu g\,L^{-1}$ levels were in the range of 82–113%.

Keywords: Room-temperature ionic liquid; Liquid–liquid microextraction; Nonylphenol; Octylphenol

1. Introduction

Despite its widespread application for organic micropollutants in water [1–3], conventional liquid–liquid extraction (LLE) is considered to be a time- and organic solvent-consuming, multistage extraction process. To overcome these drawbacks, some interest has been focused on miniaturizing conventional liquid–liquid extraction, such as liquid–liquid microextraction (LLME) [3–10], i.e. extracting analytes into small volumes (0.6–4 mL) of organic solvents; liquid-phase microextraction (LPME) [11–14], i.e. extracting analytes into a single drop (1–10 μL) of organic solvents (suspended from the tip of a microsyringe needle) or into small volumes (1–50 μL) of acceptor solution (present inside the lumen of porous hollow fibres). The main advantages of these microextraction procedures compared with LLE are a reduction in extraction time and organic-solvent consumption, simplification of the extraction operation, elimination

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of the concentration step, and use of small sample volumes. Consequently, the costs of analysis are low, but drop or hollow-fibre-based LPME must be performed very carefully because of small volumes of organic solvents (1–50 µL), while LLME has shown to be a convenient operation and an efficient alternative to conventional LLE so that LLME is frequently used in US EPA methods for sample preparation [4, 5, 15, 16].

In conventional LLME, a water sample (1–50 mL) is usually extracted with a small volume of organic solvent (0.6–4 mL) and the extract is directly injected into a capillary gas chromatography (GC) [4–10].

Room-temperature ionic liquids (RTILs), composed of organic cations and various organic or inorganic anions, are emerging as a replacement for volatile solvents traditionally used in LLE [17–22], although they cannot be concentrated because of their non-volatility. Therefore, RTILs can only be used in microextraction procedures which combine the extraction and concentration steps. In RTIL-based LPME [23, 24], a single drop of RTIL was suspended on the tip of a microsyringe needle. The analytes were extracted from the aqueous sample and into RTIL, and then the RTIL drop was retracted into the microsyringe and injected into the HPLC system for analysis. However, besides the disadvantage stated above compared with LLME, RTIL-based LPME has another problem, i.e. because of the large viscosity of RTIL, air is so easily withdrawn into the microsyringe accompanied with RTIL that it will inevitably influence the analytical results.

In RTIL-based LLE systems reported in the literature [17–21] 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]) was the most widely used RTIL owing to its unique properties, such as its ability to remain in the liquid state at room temperature (melting point 10°C), its air and water stability, immiscibility with water, and high solubility of organic compounds within. Therefore, [C_4MIM][PF_6] would be an attractive alternative to VOC-based LLME. When employed in LLME, the negligible vapour pressure of [C_4MIM][PF_6] is an important advantage over the volatility of traditional volatile organic compounds (VOCs) that can lead to worse reproducibility, low method recovery [3, 7] and troublesome steps of periodic venting to release excess pressure during extraction [3].

Alkylphenol ethoxylates (APEs) are non-ionic surfactants used widely in industrial and domestic cleaning products. The 4-nonylphenol (4-NP) and 4-*tert*-octylphenol (4-*t*-OP) are two major degradation products of APEs. Being more persistent than their parent compounds and having oestrogenic effects, 4-NP and 4-*t*-OP have been of increasing concern in recent years [25, 26]. So, the need for the quantitative determination of 4-NP and 4-*t*-OP from environmental samples has emerged, and many related analytical methods have been reported [27–29].

In this article, the usage of RTIL [C_4MIM][PF_6] in LLME for the determination of 4-NP and 4-*t*-OP in water by HPLC has been evaluated. The recommended procedure was applied to actual water samples from a river and a sewage-treatment plant.

2. Experiment

2.1 *Equipment*

The HPLC systems LC-10AT (Shimadzu, Tokyo) were equipped with a fluorescence detector RF-10A XL (Shimadzu, Tokyo) set at 223 nm excitation and 302 nm emission, a pump LC-10AT VP (Shimadzu, Tokyo), and a Class-VP ChemStation program for LC used to process chromatographic data. The chromatography was carried out on a Shimadzu Shim-pack VP-ODS column (150 × 4.6 mm i.d., 5 µm particle size). The mobile phase was acetonitrile–water (80 : 20 v/v), and the flow rate was 1 mL min^{-1}.

A constant-temperature vortex THZ-C was supplied by Taicang (Jiangsu, China). The vibration speed and temperature were set at 120 rpm and 25°C, respectively, in all tests.

2.2 *Chemicals*

HPLC-grade methanol and acetonitrile were obtained from Scharlau (Barcelona). Reagents for synthesis of $[C_4MIM][PF_6]$ including 1-methylimidazole (99%), 1-chlorobutane (99%), and hexafluorophosphoric acid (60 wt% solution in water) were from Acros Organics (Geel, Belgium) and used as received. Hexafluorophosphoric acid is a corrosive and toxic chemical, and must be handled with care. All the other chemicals were analytical-grade reagents. Ultrapure water was produced on the system of Millipore S.A.S. 67120 Molsheim (France). The pH value of aqueous solutions was adjusted using HCl or NaOH. 4-NP (100.0%), a mixture of isomers, and 4-*t*-OP (99.0%) were purchased from Dr. Ehrenstorfer (Ausburg, Germany). These were dissolved respectively in methanol at 1 mg mL^{-1} concentration as stock solutions. Working standards of mixtures of 4-NP and 4-*t*-OP were prepared by diluting aliquots of the stock solutions in methanol. Spiked water samples were prepared from stock standard solutions, ensuring a methanol content of less than 1% in the final aqueous solution.

The river water sample was collected from the Haihe River in Tianjin, and the wastewater sample was from the Xinshuiyuan sewage-treatment plant in TEDA district of Tianjin. All samples were filtered through 0.45 µm membranes before use.

2.3 *RTIL $[C_4MIM][PF_6]$ synthesis*

$[C_4MIM][PF_6]$ was prepared as published elsewhere [17]. Briefly, $[C_4MIM][PF_6]$ was prepared by reacting equal molar amounts (0.3 mol) of 1-methylimidazole and 1-chlorobutane in a round-bottomed flask fitted with a reflux condenser by heating and stirring at 70°C for 48 h. The resulting viscous liquid 1-butyl-3-methylimidazolium chloride ($[C_4MIM]Cl$) was washed three times with ethyl acetate and then heated to 70°C under vacuum. Hexafluorophosphoric acid (0.17 mol) was added slowly to a mixture of $[C_4MIM]Cl$ (0.15 mol) in 100 mL of water. After stirring for 12 h, the lower ionic liquid was washed with water until the washings were no longer acidic. $[C_4MIM][PF_6]$ was then heated under vacuum at 70°C to remove any excess water.

2.4 *Extraction procedure*

A 20 mL water sample was transferred to a 20 mL graduated centrifugal tube and then adjusted the pH value to 2 by adding up to 100 µL of 2 mol L^{-1} HCl. Then, 0.4 mL of organic solvent (dichloromethane or $[C_4MIM][PF_6]$) was added, and the tube was capped. The mixture was shaken mechanically (vortex) for a certain period of time.

The organic layer was allowed to separate from the water phase for 10 min. The water phase was then removed using a disposable glass pipette, being careful not to include any organic phase. If dichloromethane was used as extraction solvent, it was evaporated to dryness using a gentle stream of clean, dry nitrogen. This step could be omitted in [C_4MIM][PF_6]. After extraction, acetonitrile was added to the extract to a final volume of 0.4 mL (calibration was checked at the volumes employed in the test in advance), in order to decrease ionic liquid viscosity. In the case of dichloromethane, 0.4 mL of acetonitrile were added. Then, 20 µL of the sample extract was injected into the HPLC system for analysis.

3. Results and discussion

3.1 *Comparison of extraction time and solvent*

Two solvents including [C_4MIM][PF_6], a typical RTIL, and dichloromethane, a typical traditional organic solvent, were compared as extraction solvents in this study. It must be noted that when dichloromethane was used as the extracting solvent, the tube caps had to be removed after the first agitation to release the excess pressure, whereas this operation was not needed for [C_4MIM][PF_6].

The results displayed in figure 1 (extracting 20 mL of water sample containing 4-NP and 4-*t*-OP at the 50 µg L^{-1} level with 0.4 mL of organic solvent) showed the effect of organic solvents and extraction time on the extraction efficiency. The extraction efficiency is defined as the fraction of analyte extracted from the water sample into the extraction solvent, i.e. n_o/n_a, where n_o is the amount of analytes in the organic phase after extraction, and n_a is the original total amount of analytes in the aqueous phase. As can be seen in figure 1, when [C_4MIM][PF_6] was used as extraction solvent, the extraction efficiency increased with increasing extraction time up to 60 min, then remained unchanged with longer times because extraction equilibrium between the two phases was reached. However, for dichloromethane, the extraction efficiency increased with increasing extraction time up to 20 min, remained unchanged for 20–30 min,

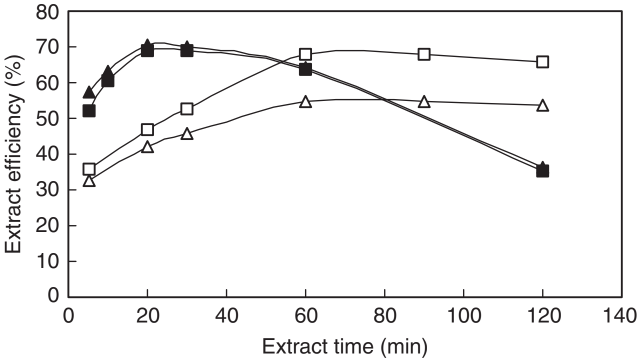

Figure 1. Effect of time on the extraction of 20 mL of 50 µg L^{-1} spiked 4-NP and 4-*t*-OP water sample with 0.4 mL of organic solvent. (▲) 4-NP, dichloromethane; (■) 4-*t*-OP, dichloromethane; (□) 4-*t*-OP, [C_4MIM][PF_6]; (△) 4-NP, [C_4MIM][PF_6].

then decreased gradually with longer extraction times. This was probably because dichloromethane is volatile, and the volume of the remaining dichloromethane decreased significantly after extraction equilibrium (20–30 min), leading to the reduction in extraction efficiency. The extraction equilibrium time in the dichloromethane–water system was much shorter than that in the [C_4MIM][PF_6]-water system, because the viscosity of dichloromethane (0.43 mPa s) was much lower than that of [C_4MIM][PF_6] (312 mPa s) [17], and thus the mass transfer rate was faster in dichloromethane than in [C_4MIM][PF_6]. It is clear from figure 1 that dichloromethane possessed a higher extraction efficiency for both 4-NP and 4-*t*-OP than [C_4MIM][PF_6].

The extraction times of 60 min for [C_4MIM][PF_6] and 20 min for dichloromethane were adopted in the following study. Although the extraction time for [C_4MIM][PF_6] was relatively long, a large number (15–20) of samples may be extracted simultaneously because of the simplicity and low cost of the extraction device. In the RTIL-based LPME [23, 24] mentioned above, a microlitre microsyringe was used as the extraction device, which is so expensive that only a few parallel extractions can be conducted. By contrast, the RTIL-based LLME method presented here, which uses a very cheap glass tube instead of a microlitre microsyringe, is suitable for handling a large number of batches of water samples simultaneously. Therefore, the cost of the LLME technique in the present work is much lower than that of the LPME reported in the literature [23, 24].

3.2 *Repeatability*

Although dichloromethane had a higher extraction efficiency than [C_4MIM][PF_6], repeatability experiments, measured by five repeated extractions of 50 $\mu g\,L^{-1}$ of spiked 4-NP and a 4-*t*-OP water sample with 0.4 mL of organic solvent, showed that it had a poorer precision (R.S.D. > 20%) than [C_4MIM][PF_6] (R.S.D. < 10%). This was because of the volatilization of dichloromethane leading to a poor repeatability, while [C_4MIM][PF_6] was nonvolatile. So, [C_4MIM][PF_6] was chosen as the extraction solvent for further experiments.

3.3 *Phase ratio*

The phase ratios (the aqueous phase : organic phase ratio) used in LLME in the reported literature [3–10] were usually 2 : 1 to 17 : 1, which were too low to produce adequate enrichment factors with sufficient sensitivity. So, in the present study, the phase ratio was increased by shaking 0.4 mL of [C_4MIM][PF_6] with either 10 mL or 20 mL of water sample (phase ratios 25 : 1 and 50 : 1, respectively); the results are listed in table 1.

Table 1. Influence of phase ratio on the extraction efficiency and enrichment factor of 50 $\mu g\,L^{-1}$ of 4-NP and 4-*t*-OP in water sample extracted by [C_4MIM][PF_6] for 60 min.

Analyte	Phase ratio	Extraction efficiency (%)	Enrichment factor
4-*t*-OP	1 : 25	90.2	22.5
	1 : 50	67.6	33.8
4-NP	1 : 25	78.1	19.5
	1 : 50	54.8	27.4

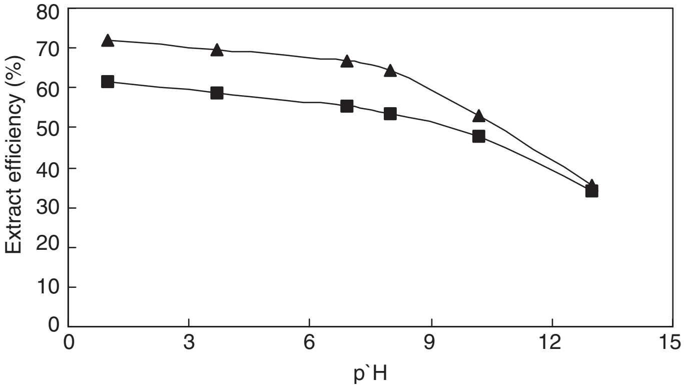

Figure 2. Effect of pH value on the extraction of 20 mL of 50 µg L^{-1} of spiked 4-NP (■) and 4-*t*-OP (▲) water sample with 0.4 mL of [C_4MIM][PF_6] for 60 min.

The extraction efficiency was found to be higher when using a 25 : 1 phase ratio, while the enrichment factor was higher when using a 50 : 1 phase ratio. The enrichment factor is defined as the ratio of C_o/C_a, where C_o is the concentration of analytes in the ionic liquid phase after extraction, and C_a is the original concentration of analytes in the aqueous phase. To increase the sensitivity of analysis, a 50 : 1 phase ratio, i.e. 20 mL of water sample with 0.4 mL of [C_4MIM][PF_6], was chosen for subsequent experiments.

It should be noted that because of the solubility of [C_4MIM][PF_6] in water (18.8 mg mL^{-1}) [19], a phase ratio greater than 50 : 1 can lead [C_4MIM][PF_6] to achieve no separation from the aqueous phase.

3.4 *Effect of pH value and salt*

The influence of pH value on the extraction of 4-NP and 4-*t*-OP with [C_4MIM][PF_6] is shown in figure 2. The extraction efficiencies decreased with increasing pH, from 1 to 13. At low pH, 4-NP and 4-*t*-OP are mainly in their neutral forms that prefer to be distributed in the organic phase. This leads to a high extraction efficiency at a low pH. On the contrary, a low extraction efficiency was obtained at a high pH, because 4-NP and 4-*t*-OP are partially in their deprotonated forms that prefer partition in the aqueous phase. Therefore, in the following studies, the water samples were adjusted to pH 2 by adding 100 µL of 2 mol L^{-1} HCl just before extraction.

In this study, the effect of salt on RTIL based LLME was investigated by adding different amounts of sodium chloride (NaCl) to the sample, and results indicated that the increase in NaCl concentration in aqueous phase, i.e. 0, 5, 10, 20 g/100 mL, had no significant influence on the extraction of 4-NP and 4-*t*-OP with [C_4MIM][PF_6]. The reason for this was not clear.

3.5 *Quantitative aspects*

On the basis of the experiments discussed above, optimum LLME of 4-NP and 4-*t*-OP was obtained by using 20 mL of water sample adjusted to pH 2 with 0.4 mL of [C_4MIM][PF_6] and shaking for 60 min. To evaluate the proposed IL-based

Table 2. Performance of IL-based LLME.

					Recovery (%) ($n = 5$)	
Analyte	Regression equation (R^2)	R.S.D. (%) ($n = 5$)	Linear range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)	$6\,\mu g\,L^{-1}$	$25\,\mu g\,L^{-1}$
4-*t*-OP	$y = 38{,}661x + 23{,}5715$ (0.9981)	3.7	1–175	0.6	85–108	90–106
4-NP	$y = 16{,}498x + 87{,}969$ (0.9948)	8.1	6–175	2	82–112	86–113

Note: LLME conditions: extracting 20 mL of water sample (pH = 2) with 0.4 mL of [C_4MIM][PF_6]; extraction time: 60 min.

LLME method, characteristics such as regression equations, linearity, repeatability, and limits of detection (LOD) were investigated under optimum conditions. Because of inefficient extraction (extraction efficiency < 80%), analytes were quantified using procedural standard calibration to compensate for incomplete extraction of the target compounds. Procedural standard calibration is a calibration method in which aqueous calibration standards are prepared in exactly the same manner as the samples described in section 2.4, i.e. spiking ultrapure water at various levels, and then performing the proposed LLME procedure to obtain the calibration standards. Thus, the procedural calibration curve was obtained, and the results are shown in table 2. It can be seen that the linearity was evaluated within the range of 6–175 $\mu g\,L^{-1}$ for 4-NP and 1–175 $\mu g\,L^{-1}$ for 4-*t*-OP, and correlation coefficients (R^2) were 0.9948 for 4-NP and 0.9981 for 4-*t*-OP. The precisions (R.S.D.) of the proposed procedure, measured by five repeated extractions of a 50 $\mu g\,L^{-1}$ spiked water sample were 8.1% for 4-NP and 3.7% for 4-*t*-OP, respectively. The calculated limits of detection ($S/N = 3$) were 2 $\mu g\,L^{-1}$ for 4-NP and 0.6 $\mu g\,L^{-1}$ for 4-*t*-OP.

It should be noted that the procedural standard calibration described above must be validated against sample matrix effects. To this end, recoveries should be calculated from real water samples in the following study.

3.6 *Real water sample analysis*

In order to test the practical applicability of the proposed method in the real world, it was applied to two aqueous samples, i.e. river water and effluent from a sewage-treatment plant. No target analytes could be found in the river-water sample, while the effluent from the sewage treatment plant contained 2.4 $\mu g\,L^{-1}$ of 4-*t*-OP. The two water samples were then spiked with the analytes at 6 $\mu g\,L^{-1}$ and 25 $\mu g\,L^{-1}$ levels (five replicates for each level). The mean recoveries of 4-NP and 4-*t*-OP shown in table 2 were in the range of 85–108% and 82–113%, respectively. It can be concluded that the procedural standard calibration described above is valid, and the RTIL-based LLME method as a sample preparation is applicable to real water samples. Figure 3 shows typical chromatograms of original and 6 $\mu g\,L^{-1}$ spiked effluent from a local sewage-treatment plant.

4. Conclusion

The RTIL-based LLME method can be considered a good alternative to conventional LLE for the determination of 4-NP and 4-*t*-OP by liquid chromatography

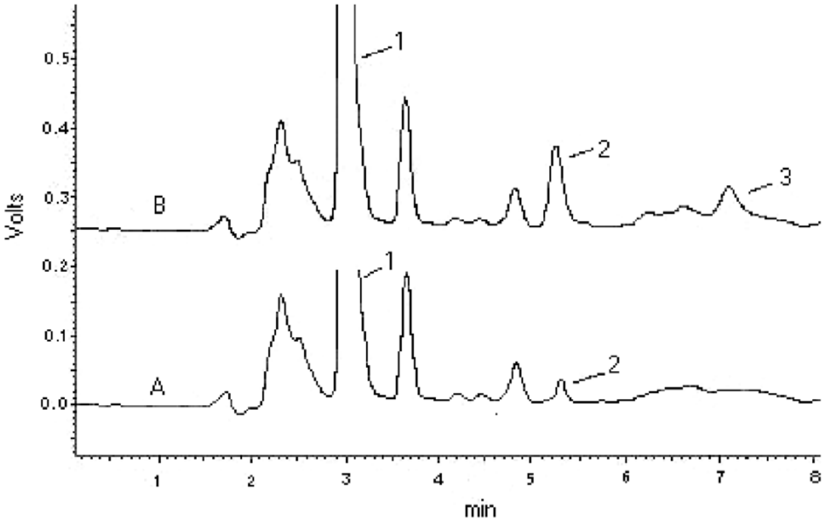

Figure 3. Typical chromatograms of effluent collected from a local sewage-treatment plant. Sample blank (1 = [C_4MIM][PF_6]; 2 = 4-*t*-OP). Sample spiked with 6 µg L^{-1} of 4-NP and 4-*t*-OP (1 = [C_4MIM][PF_6]; 2 = 4-*t*-OP; 3 = 4-NP).

in environmental aqueous samples. The optimized method allows analytes in water to be determined at µg L^{-1} levels. Compared with conventional LLE, the RTIL-based LLME is rapid, involves simple handling, is cheap, has no preconcentration step, and avoids environmental problems derived from the use of large volumes of organic solvents.

Although the LOD of the analytes are somewhat high in the proposed method, the advantages of this technique make it suitable for screening analysis in routine work. Further investigations are required for the use of RTILs other than is [C_4MIM][PF_6], which could enhance the sensitivity by using larger aqueous : organic phase ratios, if RTILs are less soluble in water than [C_4MIM][PF_6].

The overall time of extraction and analysis is about 90 min per sample. Large parallel experiments could be conducted simultaneously. Furthermore, RTILs based LLME is compatible with reversed-phase HPLC while LLME based on the commonly used organic solvents is only compatible with GC.

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References

[1] USEPA Method 507. American Society for Testing and Materials, Philadelphia, PA (1995).
[2] USEPA Method 508. American Society for Testing and Materials, Philadelphia, PA (1995).
[3] USEPA Method 8321.a. American Society for Testing and Materials, Philadelphia, PA (1996).

[4] USEPA Method 552.3. American Society for Testing and Materials, Philadelphia, PA (2003).
[5] USEPA Method 556. American Society for Testing and Materials, Philadelphia, PA (1998).
[6] J. Beltran, F.J. Lopez, M. Foreada, F. Hernandez. *Anal. Chim. Acta*, **125**, 356 (1997).
[7] F.J. Lopez, J. Beltran, M. Forcada, F. Hernandez. *J. Chromatogr. A*, **25**, 823 (1998).
[8] M. Guidottia, R. Giovinazzob, O. Cedroneb, M. Vitalib. *Environ. Int.*, **23**, 26 (2000).
[9] X.Y. Feng. *Water Res.*, **35**, 1599 (2001).
[10] F.W. Wu, W. Gabryelski, K. Froese. *Analyst*, **127**, 1318 (2002).
[11] Y. He, H.K. Lee. *Anal. Chem.*, **69**, 4634 (1997).
[12] A.L. Theis, A.L. Waldack, S.M. Hansen, M.A. Jeannot. *Anal. Chem.*, **73**, 5651 (2001).
[13] S. Muller, M. Moder, S. Schrader. *J. Chromatogr. A*, **99**, 985 (2003).
[14] M. Charalabaki, E. Psillakis, D. Mantzavinos, N. Kalogerakis. *Chemosphere*, **60**, 690 (2005).
[15] USEPA Method 551. 1. American Society for Testing and Materials, Philadelphia, PA (1995).
[16] USEPA Method 8011. American Society for Testing and Materials, Philadelphia, PA (1992).
[17] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers. *Chem. Commun.*, 1765 (1998).
[18] Sheng Dai, Y.H. Ju, C.E. Barnes. *J. Chem. Soc., Dalton Trans.*, 1201 (1999).
[19] S. Chun, S.V. Dzyuba, R.A. Bartsch. *Anal. Chem.*, **73**, 3737 (2001).
[20] A.G. Fadeev, M.M. Meagher. *Chem. Commun.*, 295 (2001).
[21] A.E. Visser, R.P. Swatloski, S.T. Griffin, D.H. Hartman, R.D. Rogers. *Separ. Sci. Technol.*, **36**, 785 (2001).
[22] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davies, R.D. Rogers. *Environ. Sci. Technol.*, **36**, 2523 (2002).
[23] J.F. Liu, Y.G. Chi, G.B. Jiang, C. Tai, J.F. Peng, J.T. Hu. *J. Chromatogr. A*, **143**, 1026 (2004).
[24] J.F. Liu, G.B. Jiang, Y.G. Chi, Y.Q. Cai, Q.X. Zhou, J.T. Hu. *Anal. Chem.*, **75**, 5870 (2003).
[25] G.J. Moffat, A. Burns, J.V. Millery, R. Joinerz, J. Ashby. *Regul. Toxicol. Pharmacol.*, **34**, 182 (2001).
[26] M. Vitali, F. Ensabella, D. Stella, M. Guidotti. *Chemosphere*, **57**, 1637 (2004).
[27] P. Voogt, K. Beer, F. Wielen. *Trends Anal. Chem.*, **16**, 584 (1997).
[28] U. Bolz, W. Korner, H. Hagenmaier. *Chemosphere*, **40**, 929 (2000).
[29] A. Latorre, S. Lacorte, D. Barcelo, M. Montury. *J. Chromatogr. A*, **251**, 1065 (2005).