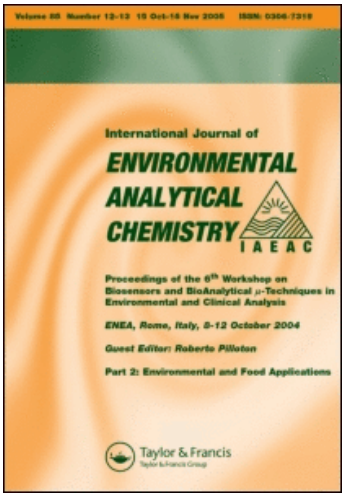

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Trace determination of phthalate esters in river water by solvent sublation followed by high-performance liquid chromatography-ultraviolet detection

Liu Guo[a]; Huiru Dong
[a] College of Science, Beijing University of Chemical Technology, Beijing, P.R. China

To cite this Article Guo, Liu and Dong, Huiru(2009) 'Trace determination of phthalate esters in river water by solvent sublation followed by high-performance liquid chromatography-ultraviolet detection', International Journal of Environmental Analytical Chemistry, 89: 5, 357 — 365
To link to this Article: DOI: 10.1080/03067310802603966
URL: http://dx.doi.org/10.1080/03067310802603966

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 5, 20 April 2009, 357–365

Taylor & Francis
Taylor & Francis Group

Trace determination of phthalate esters in river water by solvent sublation followed by high-performance liquid chromatography-ultraviolet detection

Liu Guo and Huiru Dong*

College of Science, Beijing University of Chemical Technology, Beijing, P.R. China

(*Received 23 July 2008; final version received 5 November 2008*)

A novel method for separating and enriching trace phthalate esters (PAEs) in river water by solvent sublation and their determination by high-performance liquid chromatography (HPLC) has been developed. The optimal conditions of the solvent sublation were obtained, that is *n*-hexane as the sublation solvent, pH 7 of the solution, a nitrogen flow rate of 70 mL min^{-1} and sublation time of 70 min. The floated product under the optimal conditions was determined by HPLC. In the process of HPLC analysis, an Eclipse XDB-C_{18} chromatographic column was used, and mobile phase consisted of acetonitrile and water using gradient elution, and the flow rate was 1.00 mL min^{-1}. The proposed method was applied to determine eight PAEs in the river water from Fangshan District, Beijing; the recoveries ranged from 76.9 to 120.4%, RSD values from 2.63 to 9.71%, and limit of detection values ranged from 0.001 (for diethyl phthalate and butyl benzyl phthalate) to 0.225 μg L^{-1} (for dimethyl phthalate and dicyclohexyl phthalate).

Keywords: phthalate esters; solvent sublation; high-performance liquid chromatography; river water

1. Introduction

Phthalate esters (PAEs) are widely used in the industry as plastic additives. They make the plastic flexible through weak secondary molecular interactions with polymer chains. They can be released easily from products and migrate into environment [1]. Several PAEs have been identified as endocrine disruptors [2]. Evaluation and monitoring of these compounds are important, due to their potential risks for human health and environment. There have been a variety of pre-concentration techniques, such as liquid–liquid extraction (LLE) [3,4] and solid-phase extraction (SPE) [5,6]. Nevertheless, LLE is time-consuming, requires large amounts of organic solvents that are potentially toxic, and is difficult to automate. SPE uses much less solvent than LLE but can be relatively expensive [7].

Solvent sublation was originally introduced by Sebba [8] as an auxiliary method to ion flotation. It is a kind of adsorptive bubble separation technique, in which the hydrophobic compounds in water are adsorbed on the bubble surfaces of an ascending gas stream and then collected in an immiscible liquid layer placed on top of the water column. This method with its advantages of simultaneous separation and enrichment, attracts

*Corresponding author. Email: donghr@mail.buct.edu.cn

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802603966
http://www.informaworld.com

much attention in the fields of environmental analysis and wastewater treatment [9–15] recently.

Solvent sublation has practical and theoretical advantages over other extraction methods (such as LLE). First, the solvent sublation process is not limited by the equilibrium constant, so the recovery of trace substances can eventually reach 100%. Secondarily, in solvent sublation, the possibility of easy handling of large volumes of aqueous samples exists, whereby the enrichment factors can easily exceed ratios of 100 : 1, thus making the techniques of great potential interest for the analysis of natural, residual and marine waters for trace substances. In addition, the phase stirring process associated with LLE frequently leads to the formation of undesirable emulsions. In the solvent sublation process, however, emulsion formation is negligible owing to the absence of phase mixing process, so that the solvent sublation method can offer high selectivity, simplicity and rapidity.

In this article, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-propyl phthalate (DPrP), dibutyl phthalate (DBP), diamyl phthalate (DAP), butyl benzyl phthalate (BBP), dicyclohexyl phthalate (DCHP) and bis(2-ethylhexyl) phthalate (DEHP) were selected as model compounds, the structures of these PAEs have hydrophobic groups, they can be adsorbed on the bubble surfaces of an ascending gas stream and then dissolved in some kinds of organic solvent placed on the surface of the sample solution. Therefore, they are suitable for solvent sublation. The effects of organic solvent, pH of the solution, nitrogen flow rate and sublation time on the efficiency of PAEs solvent sublation were investigated in detail. The floated product in the optimal conditions was measured by high-performance liquid chromatography (HPLC). The proposed method was applied to real water sample with good result.

2. Experimental

2.1 *Reagents and samples*

Isoamyl alcohol, *n*-octanol, *n*-hexane, hydrochloric acid and sodium hydroxide (Beijing Chemical Reagent Factory, China) were all of analytical-reagent grade. Methanol (Tianjing Xihua Special Reagent Factory, China) and acetonitrile (Fisher Co., USA) were chromatographic grade. The individual PAE standards including DEP (purity 99.9%), DPrP (purity 99.7%), BBP (purity 99.9%), DAP (purity 99.9%), DCHP (purity 99.9%) and DEHP (purity 99.9%), were obtained from Tianjin Jinke chemical graduate school. Standard stock solutions of PAEs ($1.0\,mg\,mL^{-1}$) were prepared by exactly weighing and dissolving corresponding compounds in methanol, and stored in a refrigerator at 4°C. Standard solutions ($100\,\mu g\,L^{-1}$) were freshly prepared by diluting the standard stock solutions with deionised water before each use. The water sample was obtained from the Manshuiqiao river in Fangshan District, Beijing.

2.2 *Apparatus*

A Mettler Toledo 320-S pH meter (Mettler, Switzerland) was used to determine the pH of the solution. A U-3010 ultraviolet-visible spectrophotometer (Hitachi, Japan) was used to acquire the absorption spectrum. An AB204-N electron balance (Mettler, Switzerland) was used to weigh. An Agilent 1100 series HPLC (USA) equipped with ultraviolet-visible detector was used for qualitative and quantitative analysis of the floated product.

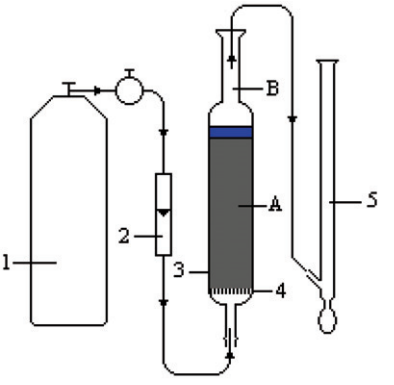

Figure 1. Solvent sublation apparatus. 1: Nitrogen cylinder; 2: pin-type flowmeter; 3: flotation cell; 4: sintered glass disk (G_4 porosity); 5: soap-bubble flowmeter.

Figure 1 shows the solvent sublation apparatus. The apparatus consists of a glass cylinder equipped with a sintered glass disk (G_4 porosity) at the bottom to generate small bubbles. The disk is connected to a N_2 gas cylinder equipped with a pressure regulator by a fine pressure needle valve for controlling the gas flow. For accurately measuring the gas flow rate through the cylinder, a soap-bubble flowmeter was inserted into the cylinder. The cylinder, with an inner diameter of 4.5 cm of part A and a capacity of 1000 mL, is designed for flotation. Sample solution is transferred to the flotation cell, then a suitable organic solvent is added to the top of the sample solution with a volumetric pipet. After flotation, deionised water is added to the top of cylinder to make the organic phase rise to part B, which has an inner diameter of 2.0 cm and a capacity of 15 mL, from which it can be easily removed. Finally, when the layers separated, the organic phase is taken into a volumetric flask with a dropping pipet, and marked with the organic solvent.

2.3 *Solvent sublation procedure*

A total of 1000 mL of water sample was placed in a 2000 mL beaker, and adjusted to pH 7 with 0.1 mol L^{-1} hydrochloric acid and 0.1 mol L^{-1} sodium hydroxide solutions. This solution was transferred to the flotation cell of the solvent sublation apparatus (Figure 1), then 10.00 mL of *n*-hexane added in, and PAEs were floated by bubbling nitrogen gas at the flow rate of 70 mL min^{-1} from the bottom of the cell for 70 min and extracted into 10.00 mL of *n*-hexane on the surface of the sample solution. After flotation, the *n*-hexane phase was transferred to a 10 mL volumetric flask, and marked with *n*-hexane. The floated product in the *n*-hexane phase was determined by HPLC.

2.4 *HPLC analysis*

The qualitative and quantitative analysis of the floated product in the *n*-hexane phase was performed with an Agilent 1100 series chromatograph. Analytes were separated on a 150×4.6 mm, 5 μm particle, Eclipse XDB-C_{18} reversed-phase column with water–acetonitrile as mobile phase (using gradient elution) at a flow rate of 1.00 mL min^{-1}. In the gradient elution, 60% acetonitrile (v/v) at the beginning, then linearly increased to

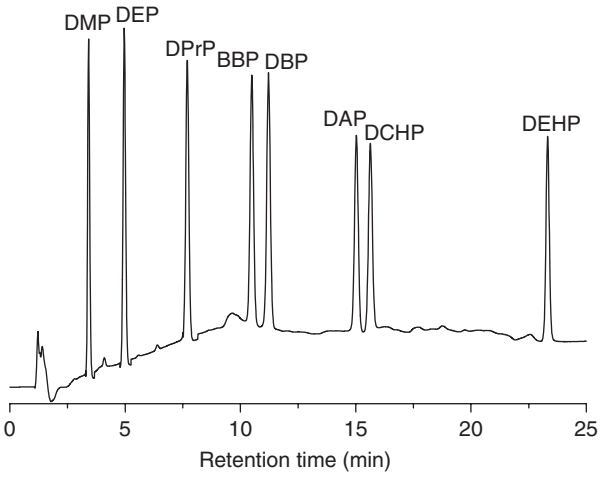

Figure 2. Chromatogram of standard mixture solution.

100% acetonitrile at 20 min and kept until 25 min. The injection volume of the *n*-hexane phase for sample and standard solutions was always 10 μL and the detection wavelength was 224 nm. Before use the mobile phase was filtered through a membrane filter (0.45 μm). The system was controlled by a computer and Chemstation software from Agilent. All chromatographic analysis was performed at room temperature. Under the selected chromatographic conditions the chromatogram for the mixture of eight PAEs was shown in Figure 2. It can be seen that eight analytes were separated within 25 min.

3. Results and discussion

3.1 *Optimisation of the solvent sublation parameters*

In this work, the sublation efficiency of PAEs in the standard solutions was used for optimising the parameters affecting the PAE solvent sublation. The sublation efficiency of PAEs can be calculated by use of the following equation:

$$E = \frac{C_i}{C_0} \times 100\%$$

In the formula, E is the sublation efficiency, C_i is the concentration of the *n*-hexane phase after flotation and C_0 is the concentration of the *n*-hexane phase when all of the PAEs (100%) are transferred from the aqueous phase into the organic phase. The concentration of PAEs in the *n*-hexane phase were determined by HPLC using an external standard method.

3.1.1 *Absorption spectra*

The maximum absorbances were at 224 nm for DMP, DEP, DPrP, DBP, DAP, DCHP and DEHP, and 213 nm for BBP. In this work, 224 nm was selected as the measurement wavelength for the ultraviolet-visible detector.

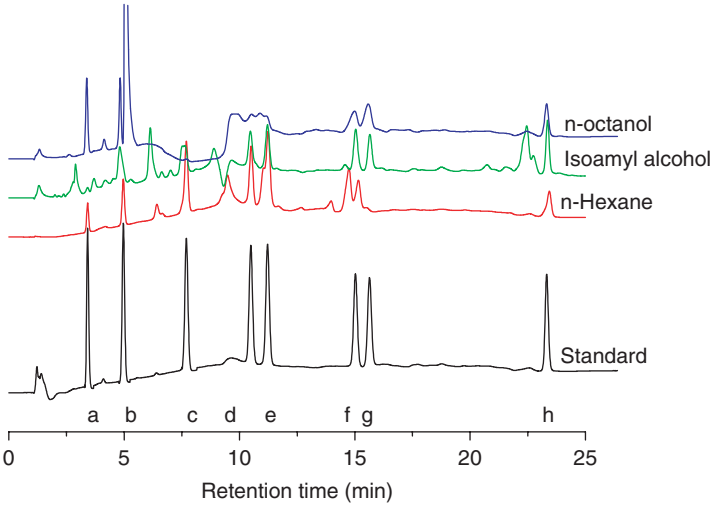

Figure 3. Effect of sublation solvents. a: DMP; b: DBP; c: DPrP; d: BBP; e: DBP; f: DAP; g: DCHP; h: DEHP.

3.1.2 *Effect of sublation solvent*

There are some restrictions in choosing a sublation solvent. That is, the solvent should have high affinity with PAEs, be lighter than a sample solution, and have a low volatility. For efficient sublation, *n*-hexane, *n*-octanol and isoamyl alcohol were investigated under the experimental conditions of pH 7 of the solution, a nitrogen flow rate of 40 mL min^{-1} and sublation time of 30 min. The experimental results (Figure 3) showed that of all the solvents the best solvent was *n*-hexane, and the next was isoamyl alcohol. Therefore, *n*-hexane was selected as the sublation solvent of PAEs in this work.

3.1.3 *Effect of pH*

The effect of pH from 1 to 13 was investigated by addition of suitable hydrochloric acid solution or sodium hydroxide solution. The PAEs in the standard solutions were floated into 10.00 mL of *n*-hexane at the flow rate of 40 mL min^{-1} for 30 min at each pH. As shown in Figure 4, the sublation efficiency of PAEs increased slightly with the increase of pH in the pH range of 1–7, and the maximum sublation efficiency was observed at pH 7. When the pH was higher than 7, however, the sublation efficiency decreased. Therefore, pH 7 was selected as an optimal pH for the efficient sublation.

3.1.4 *Effect of nitrogen flow rate*

As is well known, the bubbling of nitrogen is very important in solvent sublation because the bubbles can float the hydrophobic analytes to the surface of the solution. As the bubbles rise through the gas diffuser, the hydrophobic analytes are adsorbed at the gas–liquid interface and then extracted into the organic phase on the surface of the sample solution. Generally, the rate of gas–liquid interfacial area generation can be increased by generating smaller bubbles via a gas diffuser with smaller porosity or by increasing the gas flow rate. However, it is recommended that too high gas flow rates are to be avoided

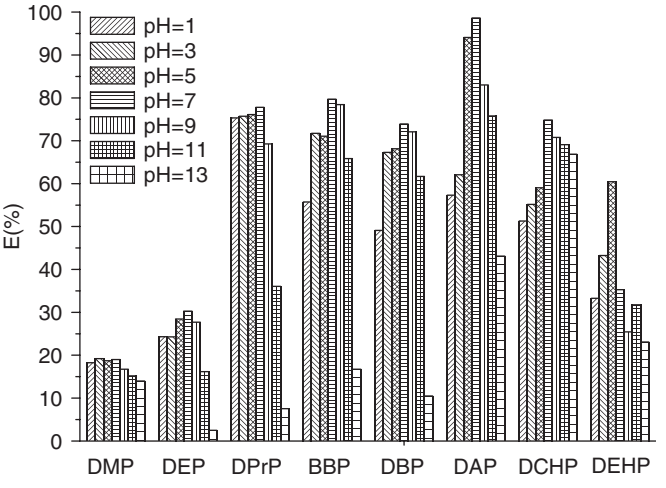

Figure 4. Effect of pH of the solution.

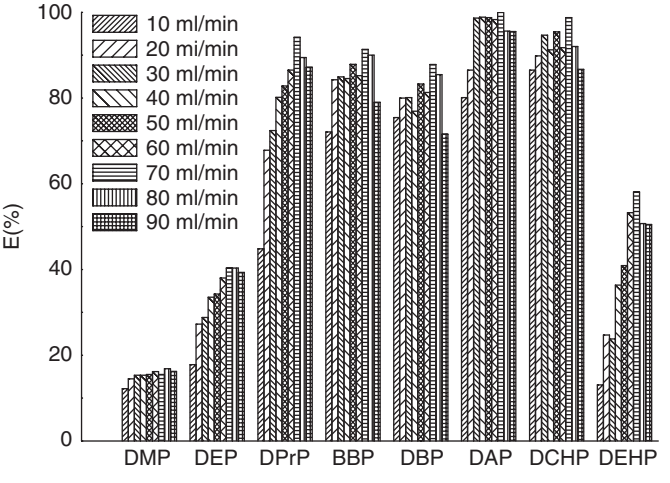

Figure 5. Effect of nitrogen flow rate.

because of a turbulent mixing at the solvent–aqueous solution interface. Such a mixing can promote the re-dissolution of the hydrophobic analytes in the aqueous phase.

As shown in Figure 5, the sublation efficiency of PAEs increased with increasing nitrogen flow rate, however, the maximum efficiency was obtained at $70\,mL\,min^{-1}$, when the nitrogen flow rate higher than $70\,mL\,min^{-1}$, the efficiency decreased slightly. Therefore, the nitrogen flow rate could be fixed at $70\,mL\,min^{-1}$ in all subsequent experiments.

3.1.5 *Effect of sublation time*

As shown in Figure 6, the sublation efficiency of PAEs increased with increasing sublation time, however, when the sublation time $\geq$70 min, the efficiency reached its highest value

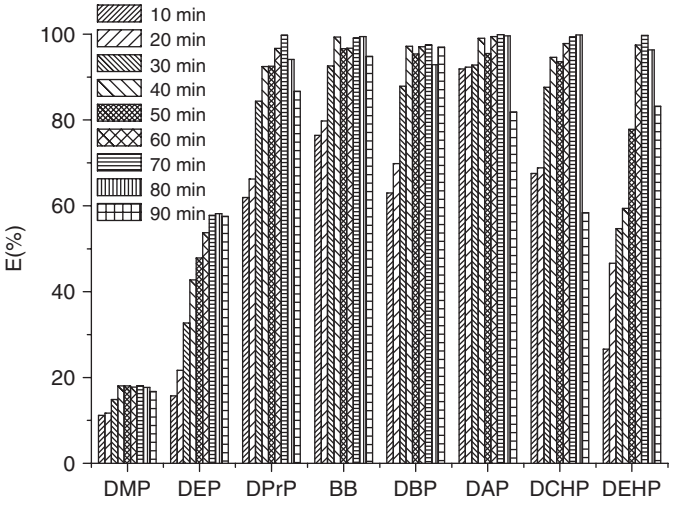

Figure 6. Effect of sublation time.

Table 1. Parameters of the calibration curves and the calculated LOD for the analytes.

Compound	Concentration range[a] ($\mu g\,L^{-1}$)	Calibration curve[b]	r[c]	LOD[d] ($\mu g\,L^{-1}$)
DMP	1.12–22.40	$y = 0.96598x - 0.03662$	0.9994	0.225
DEP	1.06–21.20	$y = 5.27545x - 0.06248$	0.9984	0.001
DPrP	1.04–20.86	$y = 17.78675x + 3.7717$	0.9994	0.034
BBP	1.23–24.72	$y = 23.17083x - 0.43752$	0.9984	0.001
DBP	1.08–21.64	$y = 17.34377x + 1.08867$	0.9991	0.007
DAP	1.03–20.54	$y = 10.9180x + 0.82237$	0.9947	0.213
DCHP	1.01–20.16	$y = 5.27545x + 0.43752$	0.9984	0.225
DEHP	1.05–20.92	$y = 11.00349x + 5.09692$	0.9990	0.136

Notes: [a]Concentration range of the studied phthalate esters; [b]Calibration curve: y is the peak area and x is the concentration of phthalate esters ($\mu g\,L^{-1}$); [c]Correlation coefficients; [d]Detection limit.

and basically remained constant because of the achievement of the thermodynamic equilibrium. The sublation time was therefore fixed at 70 min in this work.

3.2 *Calibration curve and detection limit*

The calibration curves were obtained using five standard blend solutions, which were treated under the experimental conditions optimised above. Regression analysis was used to approximate the linearity of the calibration curves, and most of the analytes were found to be linear in the tested range. The limit of detection (LOD) was calculated according to the IUPAC definition, using the equations $LOD = 3S_B/b$, where S_B is the standard deviation of the blank measurements ($n = 10$), and b is the slope of the calibration curves.

Table 1 lists the parameters of the calibration curves and the calculated LOD for the analytes.

Table 2. Determination results of the river water from Beijing Fangshan District by solvent sublation followed by HPLC-ultraviolet detection.

Phthalate esters	Content in sample ($\mu g\,L^{-1}$)	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovered ($\mu g\,L^{-1}$)	Recoveries (%)	RSD (%) ($n=3$)
DMP		4.46	10.3	5.37	120.4	
	4.93	22.3	30.5	25.6	114.7	4.48
		55.8	66.6	61.7	110.6	
DEP		4.24	5.42	5.05	119.1	
	0.37	21.2	24.3	23.9	112.7	2.63
		53.0	61.3	60.9	114.9	
DPrP		4.17	3.92	3.71	89.0	
	0.21	20.9	16.9	16.7	80.0	5.31
		52.2	44.1	43.9	84.1	
BBP		4.94	4.73	4.60	93.1	
	0.13	24.7	20.0	19.9	80.6	7.80
		61.8	51.8	51.7	83.7	
DBP		4.33	5.56	4.52	104.4	
	1.04	21.6	22.3	21.3	98.6	9.34
		54.1	47.9	46.9	86.7	
DAP		4.11	3.99	3.41	83.0	
	0.58	20.5	19.6	19.0	92.7	9.71
		51.4	52.5	51.9	100.9	
DCHP		4.03	4.57	4.21	104.5	
	0.36	20.2	20.2	19.8	98.0	3.58
		50.4	49.9	49.5	98.2	
DEHP		4.18	3.39	3.39	81.1	
	ND	20.9	16.2	16.2	77.5	2.88
		52.3	40.2	40.2	76.9	

3.3 *Real sample analysis*

The optimised experimental conditions were applied to real sample to evaluate the efficiency of the determination of PAEs by solvent sublation followed by HPLC-ultraviolet detection. The determination results are shown in Table 2. The recoveries were examined in the river water in which given amounts of analytes was determined by the proposed method. In this work, through choosing different volume added, we obtained three spiking levels, the spiking level 1 was 4.03–4.94 $\mu g\,L^{-1}$, the spiking level 2 was 20.2–24.7 $\mu g\,L^{-1}$ and the spiking level 3 was 50.4–61.8 $\mu g\,L^{-1}$. In these spiked levels, the recoveries ranged from 76.9 to 120.4% and RSD values from 2.63 to 9.71%, this accuracy of a measurement is acceptable to trace analysis. It follows that the accuracy and precision of the proposed method for trace determination of PAEs in the Manshuiqiao river water from Beijing Fangshan District, is satisfactory.

4. Conclusions

In this research, a novel and effective method for separating and enriching trace PAEs in the river water from Beijing Fangshan District by solvent sublation and its determination

by HPLC-ultraviolet detection was established. Under the selected optimal conditions the recoveries ranged from 76.9 to 120.4%, RSD values from 2.63 to 9.71%; the LOD values were 0.034 $\mu g\,L^{-1}$ for DPrP, 0.007 $\mu g\,L^{-1}$ for DBP, 0.213 $\mu g\,L^{-1}$ for DAP, 0.136 $\mu g\,L^{-1}$ for DEHP, 0.001 $\mu g\,L^{-1}$ for DEP and BBP, and 0.225 $\mu g\,L^{-1}$ for DMP and DCHP. It can be seen that the LOD values of the proposed method is lower than that of the common HPLC method, so solvent sublation is especially suitable for separating and enriching trace substances from aqueous solutions. It is, therefore, very likely that in the next few years this technique will attract much closer attention from analytical chemists.

References

[1] J.F. Jen and T.C. Liu, J. Chromatogr. A **1130**, 28 (2006).
[2] A. Gómez-Hens and M.P. Aguilar-Caballos, Trends Anal. Chem. **22**, 847 (2003).
[3] T.Y. Dai and W.M. Zhou, China Environ. Sci. **14**, 85 (1991).
[4] M.A. Jeannot and F.F. Cantwell, Anal. Chem. **69**, 235 (1997).
[5] O.S. Fakoti and A. Noma, Water Air Soil Pollut. **140**, 85 (2002).
[6] S. Jonsson and H. Boren, J. Chromatogr. A **963**, 393 (2002).
[7] J. Regueiro, M. Llompart, C. García-Jares, J.C. García-Moutelongo, and R. Cela, J. Chromatogr. A **1190**, 27 (2008).
[8] F. Sebba, *Ion Flotation* (American Elsevier, New York, 1962), p. 112.
[9] Q. Cheng and H.R. Dong, Microchim Acta **150**, 59 (2005).
[10] Y.L. Xi and H.R. Dong, Anal. Sci. **23**, 295 (2007).
[11] H.R. Dong and Q. Cheng, J. Anal. Sci. **22**, 173 (2006).
[12] Y.J. Lu, Y.S. Wang, Y. Xiong, and X.H. Zhu, Fresenius J. Anal. Chem. **370**, 1071 (2001).
[13] Y.S. Kim, J.H. Shin, Y.S. Choi, W. Lee, and Y.L. Lee, Microchem. J. **68**, 99 (2001).
[14] Y.J. Lu, J.H. Liu, J. Tang, B. Wei, and X.L. Zhang, J. Colloid Interf. Sci. **283**, 278 (2005).
[15] Y.J. Lu, X.H. Zhu, and Y.F. Peng, Sep. Sci. Technol. **38**, 1385 (2003).