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Electromembrane extraction and HPLC analysis of haloacetic acids and aromatic acetic acids in wastewater

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ABSTRACT

For the first time, haloacetic acids and aromatic acetic acids were extracted from wastewater samples using electromembrane extraction (EME). A thin layer of toluene immobilized on the walls of a polypropylene membrane envelope served as an artificial supported liquid membrane (SLM). The haloacetic acids (HAAs) (chloroacetic acid, dichloroacetic acid, and trifluoroacetic acid) and aromatic acetic acids (phenylacetic acid and *p*-hydroxyphenylacetic acid) were extracted through the SLM and into an alkalized aqueous buffer solution. The buffer solution was located inside the membrane envelope. The electrical potential difference sustained over the membrane acted as the driving force for the transport of haloacetic acids into the membrane by electrokinetic migration. After extraction, the extracts were analyzed by high-performance liquid chromatography-ultraviolet detection. The detection limits were between 0.072 and 40.3 ng L^{-1}. The calibration plot linearity was in the range of 5 and 200 μg L^{-1} while the correlation coefficients for the analytes ranged from 0.9932 to 0.9967. Relative recoveries were in the range of 87–106%. The extraction efficiency was found to be comparable to that of solid-phase extraction.

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1. Introduction

Water disinfection by chlorination is the most common method used in a water treatment plants. However, a significant problem arising from this is that organic matter (humic and fulvic compounds) and bromide/iodide compounds react during the chlorination process. An array of disinfection by-products (DBPs) results from these reactions.

DBPs are suspected human carcinogens which exhibit a potential risk of cancer after a lifetime exposure in drinking water at low concentrations. [1–3]. Today more than 500 DBPs have been found in drinking water including haloacetic acids (HAAs). They have been identified in swimming pools [4,5], natural water such as rainwater [6,7], surface water [8,] and seawater [9]. The United States Environmental Protection Agency (USEPA) sets maximum contaminant levels of 60 μg L^{-1} for five HAAs (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA)) in drinking water [7]. Thus, it is important to develop suitable analytical methods for treated and natural environmental aqueous samples for HAAs.

There are four USEPA standard methods for determining HAA concentrations in drinking water based on gas chromatography (GC) with an electron capture detector (ECD) [10–13]. GC with ECD and mass spectrometric (MS) [14,15] methods required tedious and labor intensive derivatization procedures. Due to the limitations of USEPA methods, other separation and preconcentration techniques have been developed for the determination of HAAs. Capillary electrophoresis (CE) [16] and ion chromatography (IC) have been applied to the determination of HAAs without derivatization [17]. However, development of microextraction methods for IC is challenging due to the large volume of extract that is required for analysis. In other cases, high-performance liquid chromatography (HPLC) has been used to separate nine HAAs [18,19]. The strong acidic and hydrophilic character of HAAs makes HPLC the most suitable analytical technique.

Conventional preconcentration methods such as liquid–liquid extraction (LLE), ion-exchange, and solid-phase extraction [20,21] have been used to preconcentrate HAAs from water samples. LLE processes are time-consuming, labor-intensive, and expensive. Alternatively, solid-phase microextraction (SPME) has been employed for HAA preconcentration from water [22,5,23]. Reported SPME methods require derivatization followed by analyte

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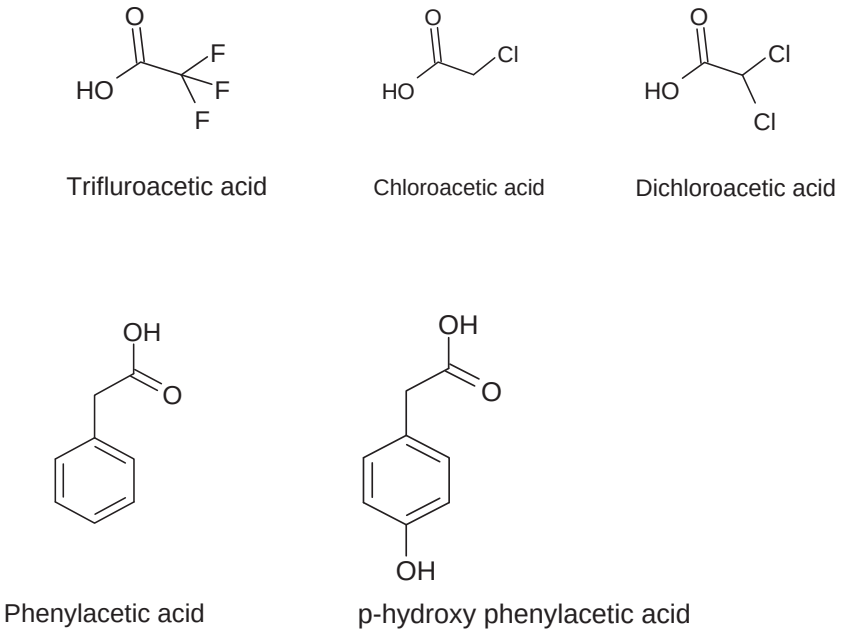

Fig. 1. Chemical structures of the studied haloacetic acids and aromatic acetic acids.

adsorption onto the SPME fiber in the headspace mode followed by GC–MS analysis.

Mitra's group developed a supported liquid membrane (SLM) extraction method which did not require a large amount of toxic solvent [24–26]. The mass transfer of analytes through SLM is usually a passive diffusion process with aid of pH gradient across the SLM. However, the extraction time to reach equilibrium is significant (60 min). To increase extraction speed in an SLM-based approach, electromembrane extraction (EME) was developed for basic drugs [27], simultaneous extraction of acid and basic drugs [28] and lead from complex samples [29]. In that method, an electrical potential was applied across the SLM which was contained within the walls of a hollow fiber membrane. Electrokinetic migration of charged chemical species across the SLM was induced by the potential difference. An EME procedure that involved the use a one-compartment polypropylene membrane envelope has also been reported [30].

In this report, the feasibility of EME, coupled with HPLC-UV for the determination of several HAAs (chloroacetic acid (CAA), dichloroacetic acid (DCAA), and trifluoroacetic acid (TFAA)), and two aromatic acetic acids (phenylacetic acid (PAA) and *p*-hydroxyphenylacetic acid (P-OH)) in water is detailed. The conditions influencing the efficiency of EME are discussed. A comparison of EME to a more established preconcentration technique, SPE, is also discussed.

2. Experimental

2.1. Chemicals and reagents

CAA was purchased from BDH Laboratory Supplies (Poole, England). DCAA, PAA, and P–OH were purchased from Sigma–Aldrich (St. Louis, MO, USA). TFAA was supplied by Fluka (Buchs, Switzerland). The chemical structures of these compounds are shown in Fig. 1. Acetonitrile was purchased from Tedia Company (Fairfield, OH, USA). Sodium dihydrogen phosphate monohydrate ($NaH_2PO_4{\cdot}H_2O$) was purchased from Merck (Darmstadt, Germany). Sodium hydroxide pellets were purchased from J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water was obtained from a Nanopure system (Barnstead, Dubuque, IA, USA). The polypropylene sheet membrane (0.45-μm pore size) was purchased from Membrana (Wuppertal, Germany).

2.2. Instrumentation

Analysis of the HAAs was performed on a Shimadzu (Kyoto, Japan) HPLC system which consisted of a LC6AD binary pump and a Shimadzu SPD-20A UV/visible spectrophotometric detector. Data was collected and processed using LC-Solution (Shimadzu) data analysis software. A Symmetry300 C_{18} column (4.6 mm × 150 mm I.D.; 5-μm particle size) from Waters (Milford, MA, USA) was used. The flow rate was 0.4 mL min^{-1} for the first 8 min and thereafter was changed to 1 mL min^{-1}. The column temperature was held at ambient (25 °C). The mobile phase was acetonitrile: 15 mM $NaH_2PO_4{\cdot}H_2O$ buffer (20:80) at pH 2.2. The detection wavelength was 210 nm.

2.3. Preparation of standards

Stock solutions (1000 mg L^{-1}) of all the HAAs were prepared in 10-mL volumetric flasks. Ten mg of each acid was accurately weighed and transferred to a 10-mL volumetric flask. Following this a combined standard of each was prepared by mixing 1 mL of each of the stock solutions.

2.4. EME procedure

The apparatus used for EME is illustrated in Fig. 2. A direct-current power supply, Microchannel Electrophoresis (CE Resources, Singapore) MCE-PS468 system with a programmable voltage, was used. Platinum wires were used as electrodes in the sample and acceptor solutions. The polypropylene membrane sheet was cut in strips, folded, and the edges were heat sealed to make envelopes. The final dimensions of each envelope were 2.5 cm × 1.4 cm. EME was performed according to the following procedure: 23 mL of ultrapure water was spiked with analytes (this served as the sample (donor solution)). The solution was stirred at 450 revolutions per minute (rpm). The polypropylene envelope

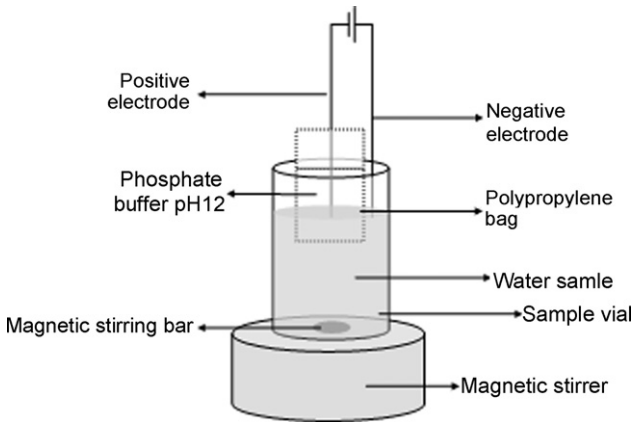

Fig. 2. Experimental setup of EME.

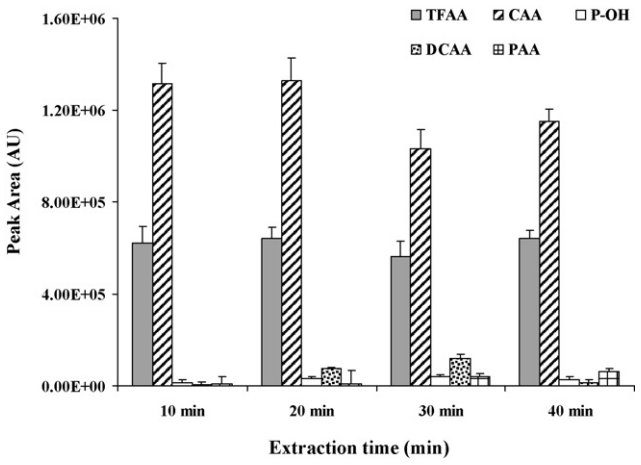

Fig. 3. Extraction time profiles of HAA and aromatic acetic acids.

was filled with 150 μL of the $NaH_2PO_4{\cdot}H_2O$ buffer (pH 12) (as the acceptor (extractant) solution). The membrane envelope was first dipped into toluene for 5 s to impregnate its wall pores. Toluene was used because it resulted in higher recoveries of the analytes compared to other solvents such as n-octanol and dichloromethane. The membrane envelope was then placed in the donor solution. The positive electrode was placed in the acceptor solution inside the membrane envelope, and the negative electrode was placed directly into the donor solution. Subsequently, voltage was applied across the membrane. After extraction, 50 μL of extract was injected into the HPLC for analysis. Each experiment was conducted in triplicate.

2.5. SPE

The optimum extraction conditions of SPE for HAAs have been reported elsewhere [31]. Briefly, Sep-Pak, Accell QMA (Waters) cartridges were equilibrated with 5 mL of sodium chloride (NaCl) solution (10%), followed by 100 mL of the HAAs-spiked water sample using a syringe pump at 1 mL min^{-1}. Following this, 10 mL of ultrapure water was injected to wash out the remaining impurities. The acids were recovered from the cartridge by eluting with 2 mL of 12.5 M sulfuric acid.

3. Results and discussion

3.1. Extraction conditions

3.1.1. Extraction time

The best extraction time for EME was determined by studying the peak areas of extracted HAAs as a function of time. In this study, the extraction equilibrium was established within the range of 10 and 40 min at room temperature (25 °C) with stirring (at 450 rpm). The amount of compounds extracted (area of chromatographic peak signals) generally increased with extraction time up to 30 min (see Fig. 3) and decreased thereafter. This is to be expected as oversaturation of analytes in the acceptor solution will lead to back-diffusion into the donor solution. Similar observations were reported by others [30–33]. Thus, an optimum extraction time of 30 min was selected for subsequent experiments.

3.1.2. Voltage

In most of the membrane-assisted extraction techniques, analyte "diffusion" due to conventional agitation plays a major role in the extraction. However, in EME, the electric potential has been proven to work as the dominant driving force. It has been demonstrated that electrokinetic migration can occur during the extraction of charged compounds; the applied potential increases the diffusion rate of the analytes to the acceptor phase [24–26]. When no voltage was applied, almost no extraction was observed [27,28]. Thus, influence of applied potential between 100 V and 500 V on the extraction efficiency was investigated (Fig. 4). The most suitable voltage was 200 V. At other voltages the analyte peak areas were lower. An increase in the applied electrical potential (from 100 to 200 V) would drive the electrokinetic migration and allow the analytes to cross the SLM faster. However, at higher voltages between 300 and 500 V, there was a decrease in the rate of extraction. This was a result of resistance to mass transfer and the build up of ions from the buffer solution at the interfaces (i.e. the boundary layer) of the artificial liquid membrane. High voltage may also lead to a degradation of the analytes. The voltage was fixed at 200 V for all experiments.

3.1.3. Sample pH

The pH of the matrix was adjusted between pH 2 and pH 12 to determine the optimum pH for HAA extraction. Extraction efficiency for aromatic acetic acids was better in basic pH. HAAs have pK_a values less than 2.86 [32,33] and are thus considered to be moderately strong acids. Ionization is more efficient if the pH of the acceptor solution is above the pK_a value of the analyte. However, when the pH is lower than the pK_a of the analyte then ionization is hindered and poorer extraction is observed. In this case, a pH value of 12 for the acceptor solution provided optimum extraction.

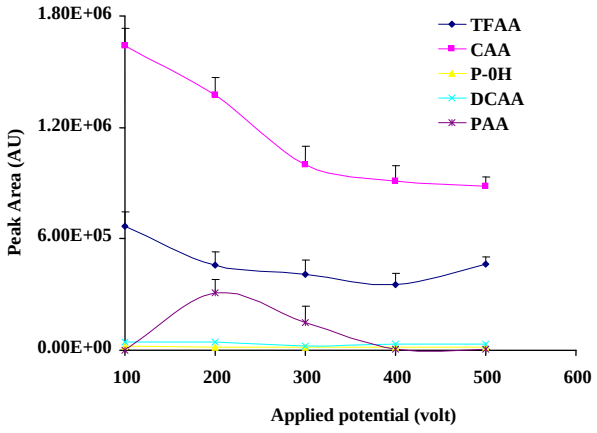

Fig. 4. Extraction efficiency on different applied potentials.

Table 1
Quantitative performance of EME.

Analyte	Linearity range ($\mu g\,L^{-1}$)	Correlation coefficient (r)	Calibration curve	RSD ($n=3$)	LOD ($ng\,L^{-1}$)
Chloroacetic acid	5–200	0.9961	$y=124376x-54589$	2.9	0.72
Trifluoroacetic acid	5–200	0.9945	$y=627620x-200506$	3.1	4.34
Dichloroacetic acid	5–200	0.9932	$y=20000x-13251$	4.9	19.3
Phenyl acetic acid	5–200	0.9928	$y=1954.9x+307.13$	6.7	19.6
p-hydroxyphenyl acetic acid	5–200	0.9967	$y=8639.2x-4207.2$	3.8	40.3

3.1.4. Ionic strength

For many analytes, aqueous solubility decreases with increasing ionic strength. Thus, an enhancement of extraction from aqueous solutions into organic solvents is observed. This phenomenon is called salting-out, and it has been used in many extraction methods [33,34]. The influence of salt on HAA extraction was investigated. Various amounts of NaCl were added to the donor solution, ranging from 3 to 15% (w/v). Fig. 5 shows the effect on extraction with respect to the NaCl concentration. As illustrated, addition of NaCl increased the extraction efficiency (from ultrapure water to 5% NaCl); however, at higher salt content (>5%), decrease in the extraction was observed. This is due to the high concentrations of salt increase the viscosity and change of conductivity of the donor solution which impeded the transportation of analyte into the acceptor solution. Therefore, the migration velocity of the ion will also change with varying ionic strength (or conductivity) correspondingly. In the present case, the highest extraction efficiency was obtained in 5% NaCl samples.

3.2. Quantitative analysis

Linearity was investigated in the concentration range of 5–200 $\mu g\,L^{-1}$. Good linearity and correlation coefficients of between 0.9932 and 0.9967 were observed (Table 1). Reproducibility studies (three replicates) were performed by using samples spiked with 5 μgL^{-1} of the working standard solution. The relative standard deviations were in the range of 2.9–6.7% (Table 1).

Limits of detection (LODs) of the acetic acids and aromatic acidic acids, calculated based on a signal to noise (S/N) ratio of 3, were in the range of 0.72–40.3 $ng\,L^{-1}$. The LODs obtained for HAAs were comparable to LLE-GC-ECD (USEPA Method 552-1), 0.0074–0.14 $\mu g\,L^{-1}$ [11]; LLE-GC-ECD (USEPA Method 552-3), 0.012–0.17 $\mu g\,L^{-1}$ [13]; liquid-phase microextraction-GC-ECD, 0.1–18 $\mu g\,L^{-1}$ [35], SLM-HPLC-UV, 0.02–2.69 $\mu g\,L^{-1}$ [26], SPME-GC–MS, 0.01–0.4 $\mu g\,L^{-1}$ [8] and better than direct-LC-tandem MS, 7.8–36.5 $\mu g\,L^{-1}$ [36]. No recent literature values were found for PAA and P–OH. However, when compared with previously reported methods [37,38], the present EME method provided 1000-fold lower LODs.

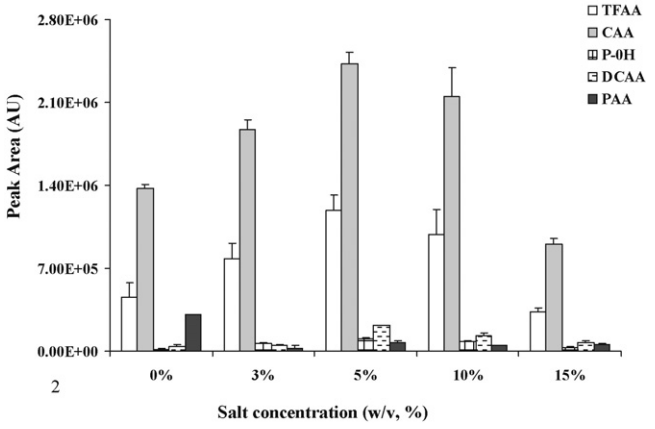

Fig. 5. Influence of salt addition on EME.

3.3. Comparison between EME and SPE

The EME method was compared to SPE for the extraction of HAAs from wastewater samples. The samples were collected from three industrial estate drains. CAA and TFAA acids were detected, and the mean concentrations were 6.2 and 2.4 $\mu g\,L^{-1}$ using EME, and 4.8 and 1.6 $\mu g\,L^{-1}$ using SPE, respectively. To assess matrix effects and compare the performance of EME and SPE, one of the wastewater samples was spiked at 5 $\mu g\,L^{-1}$ with the working standard solution and extracted. The relative recovery for a particular analyte is defined as the ratio of the HPLC peak area of the analyte in a spiked wastewater sample (representing a true environmental matrix) after extraction, compared to the peak area of the same analyte in a spiked ultrapure water sample. The relative recoveries for EME ranged between 87% and 106%, and for SPE, between 60% and 109%. For some analytes, EME provided better recoveries than SPE. Additionally, EME is a single step process whereas SPE is multistep, time consuming, and expensive. Furthermore, the EME approach was also free of memory effects since a new polypropylene envelope was used for each extraction.

4. Conclusions

In this work, electromembrane extraction (EME) using a polypropylene membrane envelope as an extraction device in combination with HPLC-UV analysis was developed. The technique was successfully applied to the analysis of HAAs from drainwater samples in an industrial area. This method exhibited good precision, reproducibility, and linear range response over a wide range of concentration. The LODs were found to be comparable with conventional methods. EME resulted in greater recovery of some HAAs in comparison to SPE. In addition, EME does not require analyte derivatization making it is less time consuming and easier to use than traditional techniques.

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References

[1] H. Shi, C. Adams, Talanta 79 (2009) 523.
[2] S.D. Richardson, Drinking Water Disinfection By-Products, in: R.A. Meyers (Ed.), The Encyclopedia of Environmental Analysis and Remediation, vol. 3, Wiley, NY, USA, 1998, p. 1398.
[3] K.P. Cantor, C.F. Lynch, M.E. Hildesheim, M. Dosemeci, J. Lubin, M. Alavanja, G. Craun, Epidemiology 9 (1998) 21.
[4] D. Martínez, F. Borrull, M. Calull, J. Chromatogr. A 835 (1999) 187.
[5] M.N. Sarrion, F.J. Santos, M.T. Galceran, Anal. Chem. 72 (2000) 4865.
[6] M. Berg, S.R. Müller, J. Mühlemann, A. Wiedmer, R.P. Schwarzenbach, Environ. Sci. Technol. 34 (2000) 2675.

[7] B.F. Scott, D. Mactavish, C. Spencer, W.M.J. Strachan, D.C.G. Muir, Environ. Sci. Technol. 34 (2000) 4266.
[8] J. Pietsch, W. Schmidt, F. Sacher, S. Fichtner, H.-J. Brauch, Fresenius J. Anal. Chem. 353 (1995) 75.
[9] S. Hashimoto, A. Otsuki, J. High Resolut. Chromatogr. 21 (1998) 55.
[10] USEPA, Method 552: Determination of Haloacetic Acids in Drinking Water by Liquid–Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detector, Environmental Monitoring and System Laboratory, Cincinnati, OH, 1990.
[11] USEPA, Method 552.2: Dalapon in Drinking Water by Ion Exchange Liquid Solid Extraction, Derivatization and Gas Chromatography with Electron Capture Detector, Environmental Monitoring and System Laboratory, Cincinnati, OH, 1995.
[12] USEPA, Method 552.1: Determination of Haloacetic Acids and Dalapon in Drinking Water by Ion Exchange Liquid Solid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection, Environmental Monitoring and System Laboratory, Cincinnati, OH, 1992.
[13] USEPA, Method 552.3: Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid–liquid Microextraction, Derivatization and Gas Chromatography with Electron Capture Detection, Environmental Monitoring and System Laboratory, Cincinnati, OH, 2003.
[14] W. Sadia, A. Pauzi, Chromatographia 69 (2009) 11.
[15] M. Jia, W.W. Wu, R.A. Yost, P.A. Chadik, P.W. Stacpoole, G.N. Henderson, Anal. Chem. 75 (2003) 4065.
[16] D. MartõÂnez, J. FarreÂ, F. Borrull, M. Calull, J. Ruana, A. Colom, J. Chromatogr. A 808 (1998) 229.
[17] R. Roehl, R. Slingby, N. Avdalovic, P.E. Jackson, J. Chromatogr. A 956 (2002) 245.
[18] T. Reemtsma, J. Chromatogr. A 1000 (2003) 477.
[19] R. Loos, D. Barcelo, J. Chromatogr. A 938 (2001) 45.
[20] D.J. Munch, J.W. Munch, A.M. Pawlecki, EPA Method 552.2, Cincinnati, OH, 1995.
[21] D. Benanou, F. Acobas, P. Sztajnbok, Water Res. 32 (1998) 2798.
[22] B. Aikawa, R.C. Burk, Int. J. Environ. Anal. Chem. 66 (1997) 215.
[23] M.N. Sarrion, F.J. Santos, M.T. Galceran, J. Chromatogr. A 859 (1999) 159.
[24] D. Kou, X. Wang, S. Mitra, J. Chromatogr. A 1055 (2004) 63.
[25] X. Wang, D. Kou, S. Mitra, J. Chromatogr. A 1089 (2005) 39.
[26] X. Wang, C. Saridara, S. Mitra, Anal. Chem. Acta 543 (2005) 92.
[27] S. Pedersen-Bjergaard, K.E. Rasmussen, J. Chromatogr. A 1109 (2006) 183.
[28] C. Basheer, J. Lee, S. Pedersen-Bjergaard, K.E. Rasmussen, H.K. Lee, J. Chromatogr. A 1217 (2010) 6661.
[29] C. Basheer, S.H. Tan, H.K. Lee, J. Chromatogr. A 1213 (2008) 14.
[30] J. Lee, H.K. Lee, K.E. Rasmussen, S. Pedersen-Bjergaard, Anal. Chim. Acta 624 (2008) 253.
[31] Y. Xie, Water Res. 35 (2001) 1599.
[32] M.I.H. Helaleh, K. Tanaka, M. Mori, Q. Xu, H. Taoda, M.-Y. Ding, W. Hu, K. Hasebe, P.R. Haddad, J. Chromatogr. A 997 (2003) 133.
[33] J. Olejniczak, J. Staniewski, J. Szymanowski, Anal. Chim. Acta 535 (2005) 251.
[34] J. Olejniczaka, J. Staniewski, Anal. Chim. Acta 588 (2007) 64.
[35] P. Varanusupakul, N. Vora-adisak, B. Pulpoka, Anal. Chim. Acta 598 (2007) 82.
[36] L. Meng, S. Wu, F. Ma, A. Jia, J. Hu, J. Chromatogr. A 1217 (2010) 4873.
[37] F. Karege, W. Rudolph, J. Chromatogr. B 570 (1991) 376.
[38] M. Yamaguchi, R. Matsunaga, K. Fukuda, M. Nakamura, J. Chromatogr. B 414 (1987) 275.