Talanta 83 (2011) 1711–1715

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A new device for magnetic stirring-assisted dispersive liquid–liquid microextraction of UV filters in environmental water samples

Ping-Ping Zhang, Zhi-Guo Shi*, Qiong-Wei Yu, Yu-Qi Feng

Key Laboratory of Analytical Chemistry for Biology and Medicine (Wuhan University), Ministry of Education, Wuhan 430072, China

ARTICLE INFO

Article history:
Received 31 July 2010
Received in revised form
22 November 2010
Accepted 30 November 2010
Available online 8 December 2010

Keywords:
Dispersive liquid–liquid microextraction (DLLME)
UV filters
1-Octanol
HPLC-UV

ABSTRACT

A new method based on dispersive liquid–liquid microextraction (DLLME) in combination with high-performance liquid chromatography (HPLC) has been developed for the analysis of UV filters. A specially designed flask, which has two narrow open necks with one of them having a capillary tip, was employed to facilitate the DLLME process. By adopting such a device, the extraction and subsequent phase separation were conveniently achieved. A binary solvent system of water sample and low-density extraction solvent (1-octanol) was used for the DLLME and no disperser solvent was involved. The extraction was accelerated by magnetic agitation of the two phases. After extraction, phase separation of the extraction solvent from the aqueous sample was easily achieved by leaving the extraction system statically for a while. No centrifugation step involving in classical DLLME was necessary. The analyte-enriched phase, floating above the sample solution, was elevated and concentrated into the narrow open tip of the flask by adding pure water into it via the other port, which was withdrawn with a microsyringe for the subsequent HPLC analysis. Under the optimized conditions, the limits of detection for the analytes were in range of 0.2–0.8 ng mL^{-1} .The linearity ranges were 8–20,000 ng mL^{-1} for HB, 7–20,000 ng mL^{-1} for DB, 8–10,000 ng mL^{-1} for BP and 5–20,000 ng mL^{-1} for HMB, respectively. Enrichment factors ranging from 59 to 107 folders were obtained for the analytes. The relative standard deviations ($n = 3$) at a spiked level of 80 ng mL^{-1} were between 1.4 and 4.8%. The proposed magnetic stirring-assisted DLLME method was successfully applied to the analysis of lake water samples.

1. Introduction

Analytical instruments cannot handle complex samples such as biological, environmental and pharmaceutical ones directly. So, developing fast, simple, inexpensive and environment-friendly sample-preparation methods is becoming a critical issue in analytical chemistry [1]. The aim of sample preparation is to clean up and concentrate target analytes from complex matrices [2]. However, conventional sample-preparation methods such as liquid–liquid extraction and solid-phase extraction may not always meet the needs of saving time, materials and labour. In the past several decades, much effort has been devoted to developing new miniaturized and economical sample-preparation techniques, including solid-phase microextraction and liquid-phase microextraction (LPME), etc. [3,4].

Recently, dispersive liquid–liquid microextraction (DLLME), a newly developed LPME method, has attracted much attention due to the merits of short extraction time, ease of operation, low cost as well as high enrichment factors for analytes [5–16]. DLLME is commonly based on a ternary solvent system in which a mixture of two types of organic solvent (disperser solvent and extraction solvent (extractant)) is quickly added into target aqueous sample solutions [6]. The disperser solvents (methanol, acetone, acetonitrile, etc.), which are miscible with both aqueous and organic phases, are involved to accelerate the extraction because it can facilitate the contact between aqueous sample solution and the extractant. However, in the present of disperser solvent, the extractant is difficult to be separated from the aqueous solution unless centrifugation at a high speed for a considerable time is employed. As centrifugation needs additional instrument and cost extra time, it is a little tedious for sample preparation. Moreover, centrifugation involved DLLME cannot handle samples of large volumes because no approximate conical centrifuge tubes were readily available.

Herein, we presented a magnetic stirring-assisted DLLME based on a homemade new device. To evaluate the effectiveness of the method and the device, several UV filters in aqueous environmental samples were used as model analytes. The extraction was carried out in a binary system composed of the extractant (1-octanol) and the aqueous sample solution. No disperser solvent was present. To facilitate the mass transfer from the aqueous samples to the extractant, during extraction, magnetic stirring was involved. After extraction, the extractant was easily separated from the aque-

* Corresponding author. Tel.: +86 27 68754067; fax: +86 27 68754067.
E-mail address: shizg@whu.edu.cn (Z.-G. Shi).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.11.076

ous phase by leaving the extraction system statically for a while (5 min). No centrifugation step was necessary. Several experimental parameters, which may influence the extraction performance of the proposed method, were investigated.

2. Experimental

2.1. Chemicals and reagents

The UV filters, 4-hydroxybenzophenone (HB), 2,4-dihydroxybenzophenone (DB), benzophenone (BP) and 2-hydroxy-4-methoxybenzophenone (HMB), were purchased from Alfa Aesar (Tianjin, China). Hydrochloric acid, sodium hydroxide and sodium chloride, 1-octanol, methanol and acetic acid of analytical grade were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Ultrapure water was produced by an Aike (Chengdu, China) water purification system.

2.2. Sample preparation

Standard stock solutions of the UV filters (1000 mg L^{-1}) were prepared by dissolving each analyte in methanol and stored at 4 °C in a fridge prior to use. Working solutions were prepared daily by diluting the standard stock solutions with ultrapure water.

Environmental water samples were collected from a swimming zone in the East Lake (Wuhan, China). They were filtrated through a 0.22-μm membrane and were adjusted to the pH of 7.0 prior to DLLME.

2.3. Extraction apparatus

The extraction is achieved in a homemade device (Fig. 1). The dimensions of it are as follows: the volume is 25 ± 3 mL; Port 1 is a neck of 4 cm in length, with a capillary tip of 1.5 cm in length and 0.2 mm in diameter; Port 2 is a neck of 12 cm in length and 1.5 cm in diameter.

2.4. Extraction procedures

Firstly, 40 μL of 1-octanol was slowly injected through Port 2 into the extraction device containing 20 mL of sample solution. The mixture was magnetically agitated for 20 min. After that, the magnetic stirring was stopped and the 1-octanol floated on the aqueous sample within 5 min. By tilting the flask to keep Port 1 (Fig. 1(C)) straightforward and adding pure water into the flask through Port 2, the liquid level was elevated and the 1-octanol was concentrated in the narrow branch tip of the bottle (Port 1). Although 40 μL of 1-octanol was added for the extraction, to ensure repeatability and accuracy, 20 μL of the analyte-enriched 1-octanol was withdrawn and diluted with 80 μL of methanol for HPLC analysis. All the experiments were performed at least three times. The schematic extraction procedures were depicted in Fig. 1.

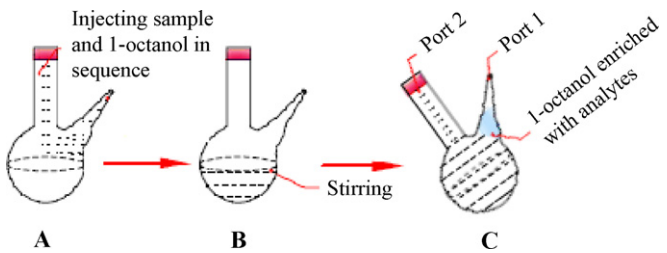
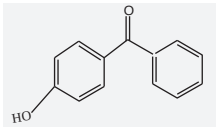
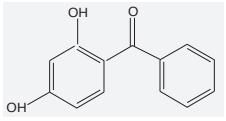
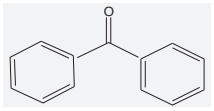
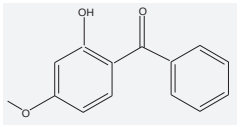


Fig. 1. Schematic of the extraction process.

Table 1
Chemical structures and some physicochemical properties of the UV filters.

Name	Structure	pK_a	Log K_{ow}
4-Hydroxybenzophenone (HB)		7.95	3.07
2,4-Dihydroxybenzophenone (DB)		7.53	2.96
Benzophenone (BP)		–	3.38
2-Hydroxy-4-methoxybenzophenone (HMB)		7.56	3.52

K_{ow}: octanol–water partition coefficient.

2.5. HPLC analysis

The experiment was carried on a HPLC system (Waters, Milford, MA, USA) equipped with a 1525 binary high-pressure pump and a 2996 photodiode array detector. An Xterra C_{18} column (150 mm × 3.9 mm, 5 μm particle size) from Waters was used for the separation of the target analytes. The mobile phase was a mixture of methanol: 1% acetic acid (60:40, v/v). The flow rate was 0.75 mL min^{-1}. The injection volume was 10 μL. The detection wavelength was set at 254 nm.

3. Results and discussion

UV filters are widely used as cosmetic additives for the protection from solar radiation. However, excessive use of them would lead to environmental pollution as well as health issues [17,18]. Generally it is difficult to directly determine this class of organic pollutants in real samples due to their low concentration and the co-existing interference [19–24]. As a result, a purification and/or enrichment procedure is necessary before analysis. Herein, a magnetic stirring assisted DLLME method was proposed for their extraction. The chemical structures and some physicochemical properties of the UV filters are given in Table 1.

3.1. Extraction optimization

Several parameters, including extraction solvent volume, extraction time, ionic strength, sample pH and stirring speed, were optimized for the extraction. An aqueous sample (20 mL) containing 80 ng mL^{-1} of each analyte was used for all experiments. If being not emphasized elsewhere, sample volume was 20 mL and each experiment was carried out in triplicate.

3.1.1. Extraction solvent volume

1-Octanol is one of the most widely used organic extraction solvents in LPME, which has shown satisfied extraction performance for various analytes. In this study, it was adopted as the extraction solvent. Its volume plays important role in DLLME because it influences not only the extraction efficiency but also the HPLC separation. 1-Octanol of different volumes ranging from 20 to 60 μL was

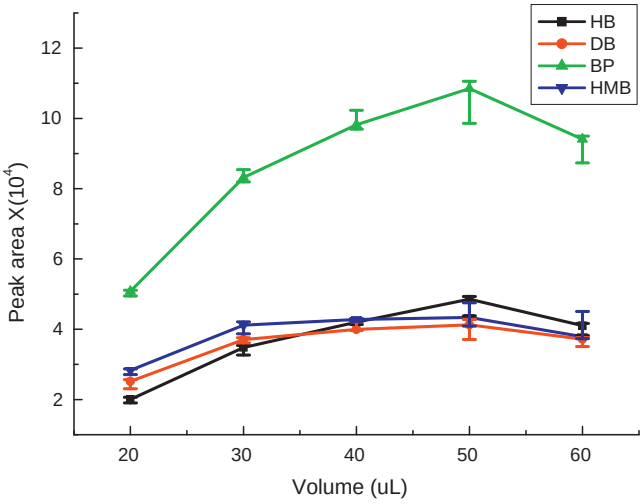


Fig. 2. Optimization of the extraction solvent volume. *Other conditions*: extraction time, 20 min; ionic strength, 0 mmol L^{-1}; pH of sample solution, 7.0; stirring speed, 1300 rpm.

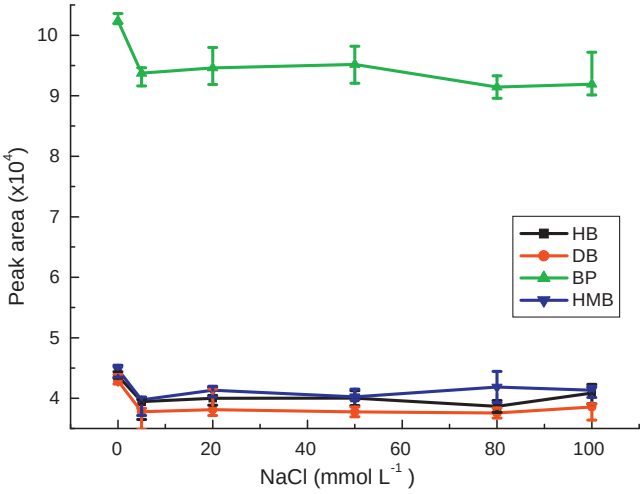


Fig. 4. Optimization of the ionic strength. *Other conditions*: extraction time, 20 min; extraction solvent volume, 40 μL; pH of sample solution, 7.0; stirring speed, 1300 rpm.

studied to examine its influence on the extraction performance. The results are shown in Fig. 2. It can be observed that the best extraction was achieved at 50 μL of 1-octanol. However, the analytes extracted in this volume displayed a poor chromatographic behavior (peak tailing), which should be ascribed to the presence of large portion of 1-octanol in the HPLC samples. When 40 μL of 1-octanol was used for the extraction, the chromatographic peaks for the analytes were quite symmetric. Therefore, 40 μL would be suitable volume for the extraction solvent.

3.1.2. Extraction time

The extraction time was investigated in the range of 2 and 50 min. The results are plotted in Fig. 3. It shows that the peak areas of all the analytes are the highest at an extraction time of 20 min. Therefore, 20 min was selected as the optimal extraction time.

3.1.3. Ionic strength

The effect of salt addition in DLLME has been widely reported. In this study, 5–100 mmol L^{-1} of sodium chloride in the sample solution was separately evaluated to determine the influence of salt addition on the extraction. The results are demonstrated in Fig. 4. It can be observed that the salt addition has little influence on the extraction performance. Therefore, no salt addition would be the best choice.

3.1.4. Sample pH values

The pH values, which can influence the molecular status of the UV filters, were investigated in the extraction. The results are displayed in Fig. 5. It can be observed that as the pH increased from 3.0 to 7.0, the peak areas for all of the analytes increased accordingly. However, as the pH increased higher than 7.0, the peak areas decreased dramatically. When the pH was lower than 7.0, the analytes probably existed in their neutral forms, which was beneficial for them to distribute into the organic phase. However, when the pH is higher than 7.0, probably the UV filters ionized in alkaline conditions, which was detrimental for their extraction. According to these results, pH 7.0 should be the optimal pH for the extraction.

3.1.5. Stirring speed

Agitation is an effective way to accelerate the mass transfer of analytes from the aqueous solution to the extraction phase. In this

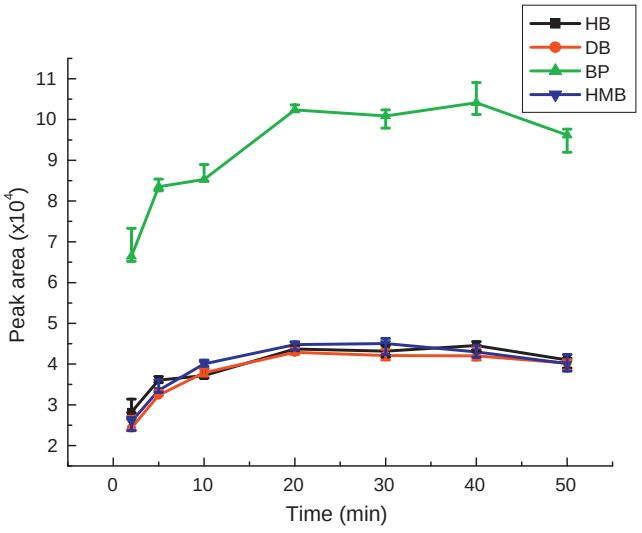


Fig. 3. Optimization of the extraction time. *Other conditions*: extraction solvent volume, 40 μL; ionic strength, 0 mmol L^{-1}; pH of sample solution, 7.0; stirring speed, 1300 rpm.

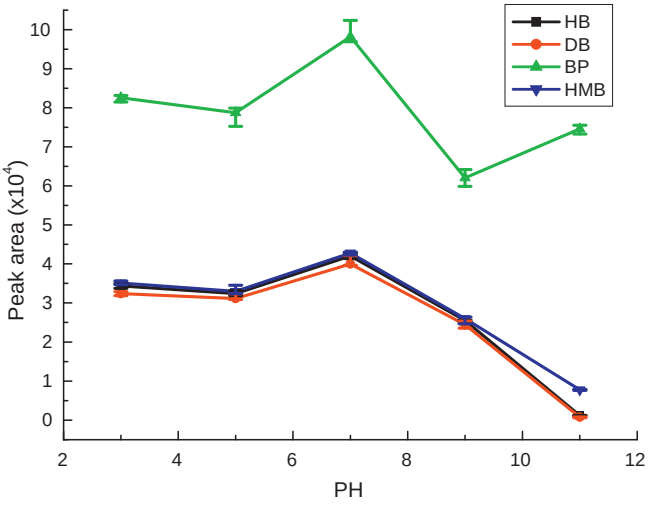


Fig. 5. Optimization of the pH value. *Other conditions*: extraction time, 20 min; extraction solvent volume, 40 μL; ionic strength, 0 mmol L^{-1}; stirring speed, 1300 rpm.

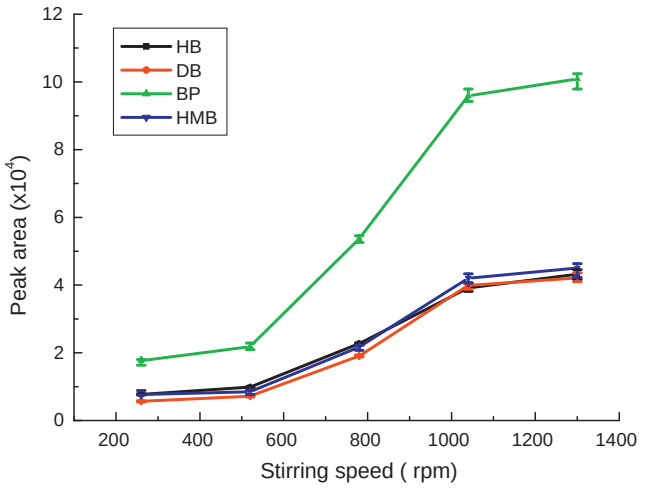


Fig. 6. Optimization of stirring speed. *Other conditions*: extraction time, 20 min; extraction solvent volume, 40 μL; ionic strength, 0 mmol L^{-1}; pH of sample solution, 7.0.

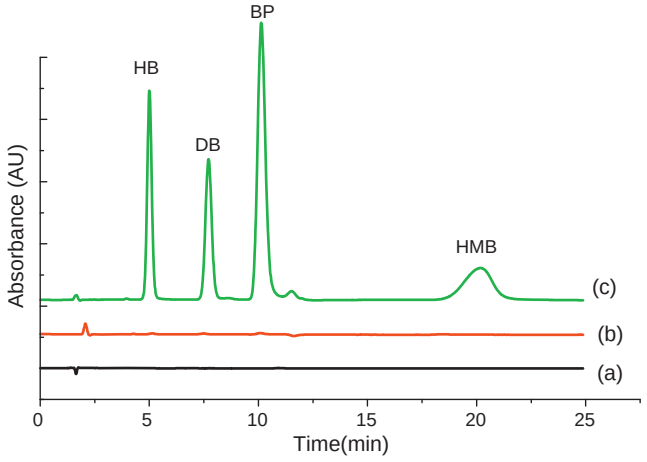


Fig. 7. Chromatograms of the UV-filters obtained by (a) DLLME-HPLC analysis of lake water directly; (b) HPLC analysis of UV filter standards at concentrations of 80 ng mL^{-1} without DLLME; (c) DLLME-HPLC analysis of lake water spiked with UV filters at concentrations of 80 ng mL^{-1}.

study, the stirring speed was investigated from 260 to 1300 rpm. It is found that as the stirring speed increased, the extraction efficiency improved significantly (as shown in Fig. 6). The fast agitation broke up the 1-octanol into fine droplets, which highly dispersed within the aqueous solution to facilitate extraction. As a result, enhanced extraction could be achieved at high stirring speed. In the present case, 1300 rpm is the maximum stirring speed of the magnetic stirrer. Therefore, this speed was used for the extraction.

Based on the above discussion, the optimal extraction conditions for the proposed method were a stirring speed at 1300 rpm, 20 min of extraction time, 1-octanol as the extraction solvent, sample pH at 7.00 and no salt addition.

3.2. Method evaluation

A series of experiments with regard to the linearity, limit of detections (LODs), enrichment factors and repeatability were performed to validate the proposed method under the optimized conditions. Sample solutions (20 mL) were prepared by spiking pure water with the UV filters at different concentration levels. The results obtained are listed in Table 2. The linearity of the method was evaluated using spiking water samples at different concentrations ranging from 5 to 20000 ng mL^{-1}. The linearity ranges were 8–20,000 ng mL^{-1} for HB, 7–20,000 ng mL^{-1} for DB, 8–10,000 ng mL^{-1} for BP and 5–20,000 ng mL^{-1} for HMB, respectively. The regression coefficients (r^2) were higher than 0.9945 for all the UV filters. The LODs, calculated at a signal-to-noise of 3, ranged from 0.2 to 0.8 ng mL^{-1}.

The repeatability was studied for three replicate experiments by spiking ultrapure water with each UV filter at a concentration of 80 ng mL^{-1}. The relative standard deviations (RSDs) were below 4.7%, illustrating the good repeatability of the proposed method. High enrichment factors ranging from 59 to 107 folders were obtained for these analytes.

Table 2
Linear range, regression data, limits of detection (LODs), relative standard deviations (RSDs) and enrichment factors of the UV filters of the DLLME method.

Analyte	Linear range (ng mL^{-1})	r^2	LOD (ng mL^{-1})	RSD[a] (%, $n = 3$)	Enrichment factor[a]
HB	8–20,000	0.9976	0.2	4.0	59
DB	7–20,000	0.9992	0.4	4.8	101
BP	8–10,000	0.9945	0.5	1.4	85
HMB	5–20,000	0.9999	0.8	4.6	107

[a] Calculated from the sample spiked at a level of 80 ng mL^{-1}.

3.3. Analysis of lake water samples

The proposed method was used to determine the UV filters in lake water samples under the optimized conditions. The lake water was filtrated and was adjusted to the pH of 7.0 prior to DLLME. It is found that these analytes cannot be detected (as shown in Fig. 7(a)), indicating the lake was free of these analytes or probably the quantity of these UV filters were below the LODs of this method. For clarity, the lake water was also analyzed by extraction with commercial SPE cartridges (AccuBond C18) (Agilent, Santa Clara, CA, USA). The sample preparation was carried out according to a previous literature [25]. By this method, there were no chromatographic signals for these UV filters, which is consistent with our DLLME method.

To test the feasibility and the accuracy of the proposed method, the processed lake water was spiked with each of the UV filters at a concentration of 80 ng mL^{-1} and then subject to the DLLME process. The result is given in Fig. 7(c). For comparison, direct determination of the analytes without extraction (each analyte at a concentration of 80 ng mL^{-1}) is displayed in Fig. 7(b). Clearly, all of the analytes were enriched. The relative recoveries were 92.2% for HB, 91.3% for DB, 97.1% for BP and 94.2% for HMB. The RSDs for them were 4.0%, 4.8%, 1.4% and 4.6% ($n = 4$) respectively, implying the established DLLME method is reliable and applicable for real sample analysis.

4. Conclusions

In the present study, a new magnetic stirring assisted dispersive liquid–liquid microextraction (DLLME) has been developed. A specially designed flask was employed to facilitate the DLLME process, in which the extraction and subsequent phase separation were conveniently achieved. The DLLME is based on a binary component solvent system of water sample and low-density extraction solvent (1-octanol). No disperser solvent was employed. As a result, 1-octanol can be easily separated from the aqueous phase without centrifugation, which may simply the extraction process and is easy to be automated.

Under the optimized extraction conditions, the limits of detection can reach ng mL^{-1} range for the UV filters. Good linearity and repeatability were also achieved. The study demonstrates that the magnetic stirring-assisted DLLME technique is a simple, effective

and easy to operate method for the sample preparation of environmental water samples.

Acknowledgements

The support of National Nature Science Foundation of China (nos. 21075091, 20605015) and the National Science Fund for Distinguished Young Scholars (no. 20625516) are gratefully acknowledged.

References

[1] A. Sarafraz-Yazdi, A.A. Amiri, Trends Anal. Chem. 29 (2010) 1–14.
[2] M. Rezaee, Y. Yamini, M. Farajii, J. Chromatogr. A 1217 (2010) 2342–2357.
[3] L. Lili, H. Xu, D.D. Song, Y.F. Cui, S. Hu, G.B. Zhang, J. Chromatogr. A 1217 (2010) 2365–2370.
[4] M.I. Leong, S.D. Huang, J. Chromatogr. A 1216 (2009) 7645–7650.
[5] M. Rezaee, Y. Assadi, M.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1–9.
[6] A. Zgoła-Grześkowiak, J. Chromatogr. A 1217 (2010) 1761–1766.
[7] P.X. Baliza, L.S.G. Teixeira, V.A. Lemos, Microchem. J. 93 (2009) 220–224.
[8] H.R. Sobhi, A. Kashtiaray, H. Farahani, M. Javaheri, M.R. Ganjali, J. Hazard. Mater. 175 (2010) 279–283.
[9] Q.X. Zhou, H.H. Bai, G.H. Xie, J.P. Xiao, J. Chromatogr. A 1188 (2008) 148–153.
[10] P. Liang, H.B. Sang, Anal. Biochem. 380 (2008) 21–25.
[11] M.B. Melwanki, M.R. Fuh, J. Chromatogr. A 1207 (2008) 24–28.
[12] H. Chen, R.W. Chen, S.Q. Li, J. Chromatogr. A 1217 (2010) 1244–1248.
[13] P. Liang, J. Xu, Q. Li, Anal. Chim. Acta 609 (2008) 53–58.
[14] T.Y. Chou, S.L. Lin, M.R. Fuh, Talanta 80 (2009) 493–498.
[15] A. Saleh, Y. Yamini, M. Faraji, M. Rezaee, M. Ghambarian, J. Chromatogr. A 1216 (2009) 6673–6679.
[16] M. Cruz-Vera, R. Lucena, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1216 (2009) 6459–6465.
[17] M.S. Díaz-Cruz, D. Barceló, Trends Anal. Chem. 28 (2009) 709.
[18] M. Schlumpf, P. Schmid, S. Durrer, et al., Toxicology 205 (2004) 113.
[19] L. Vidal, A. Chisvert, A. Canals, A. Salvador, Talanta 81 (2010) 549–555.
[20] R. Rodil, M. Moeder, J. Chromatogr. A 1179 (2008) 81–88.
[21] N. Negreira, I. Rodríguez, M. Ramil, E. Rubí, R. Cela, Anal. Chim. Acta 638 (2009) 36–44.
[22] L. Vidal, A. Chisvert, A. Canals, A. Salvador, J. Chromatogr. A 1174 (2007) 95–103.
[23] R. Rodil, S. Schrader, M. Moeder, J. Chromatogr. A 1216 (2009) 4887–4894.
[24] D.L. Giokas, V.A. Sakkas, T.A. Albanis, D.A. Lampropoulou, J. Chromatogr. A 1077 (2009) 19–27.
[25] D.A. Lambropoulou, D.L. Giokas, V.A. Sakkas, T.A. Albanis, M.I. Karayannis, J. Chromatogr. A 967 (2002) 243–253.