Talanta 85 (2011) 488–492

Contents lists available at ScienceDirect

Talanta

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

Determination of bisphenol A and naphthols in river water samples by capillary zone electrophoresis after cloud point extraction

Shuxian Zhong[a], Swee Ngin Tan[b], Liya Ge[b], Weiping Wang[a], Jianrong Chen[a,*]

[a] College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang 321004, China
[b] Natural Sciences and Science Education Academic Group, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616, Singapore

ARTICLE INFO

Article history:
Received 6 December 2010
Received in revised form 29 March 2011
Accepted 5 April 2011
Available online 12 April 2011

Keywords:
Cloud point extraction
Capillary zone electrophoresis
Bisphenol A
α-Naphthol
β-Naphthol

ABSTRACT

As a first attempt, cloud point extraction (CPE) was developed to preconcentrate bisphenol A (BPA), α-naphthol and β-naphthol prior to performing capillary zone electrophoresis (CZE) analysis. The parameters influencing the CPE efficiency, such as Triton X-114 concentrations, pH value, extraction time and temperature were systematically evaluated.

After diluting with acetonitrile, the surfactant-rich phase of CPE can be injected directly into the CE instrument. The CZE baseline separation was achieved with running buffer (pH 9.5) composed of 50 mM sodium tetraborate in 30% (v/v) methanol, and an applied voltage of 25 kV. Under the optimized CPE and CZE conditions, an preconcentration factor of 50 times could be obtained and the limit of quantification for the three analytes were found to be 1.67 μg L^{-1}, 0.80 μg L^{-1} and 0.67 μg L^{-1} for BPA, α-naphthol and β-naphthol, respectively. The proposed methods have shown to be a green, rapid and effective approach for determination of three analytes present in river water samples.

1. Introduction

Hormone disruptors are one of the major categories of environmental pollutants that scientists are concerned about [1]. As BPA is a hormone disruptor primarily used as an intermediate in the production of polycarbonate plastics, epoxy resins, flame-retardants and numerous other consumer products, it can be released into the water environment during the process [2,3]. Furthermore, BPA can also be released out from sewage-treatment plants, or the disposal of PVC materials [4]. It was observed that BPA has a significant biological impact, such as, reducing male sperm production, increasing weight of prostate and tumorigenically predisposing breast cells to cancer, even at low exposure levels [5].

Naphthol, the intermediate used in the production of dye, plastics, synthetic rubber and asbestos, has been considered as a ubiquitous environmental carcinogen [6]. α-Naphthol, one of the major degradation by-products of naphthalene and precursor of carbaryl is known to have similar toxicity as naphthalene [7]. β-Naphthol is usually produced as a by-product during α-naphthol production, and is commonly present in drinking water and industrial wastewater [8]. Naphthalene derivatives with substituent at position 2 have been found to be more toxic than those at position 1 [9].

Due to their toxicity, it is highly desirable to establish a simple, fast, low-cost, sensitive and selective analytical method to monitor concentrations of naphthalene derivatives present in the aqueous environment. Many techniques have been applied for the analysis of BPA, α-naphthol or β-naphthol, which include high performance liquid chromatography–mass spectrometry (HPLC–MS) [8,10,11], gas chromatography–mass spectrometry (GC–MS) [12] or electrochemical analysis [13]. However, analysis of these compounds in the environment is difficult, due to their low concentrations and complicated matrix effects. Hence, a pre-concentration technique is usually required, except when it is appealed to use the high cost mass spectrometry instrument. Up to now, solid-phase extraction (SPE) [14], solid-phase microextraction (SPME) [15] and Soxhlet extraction [16] have been applied to extract BPA, α-naphthol or β-naphthol from the matrices. These methods are however, eco-unfriendly, tedious, time-consuming or laborious. CPE, as a preconcentration method that is based on phase separation, has several advantages over extraction methods that used without organic solvents. These advantages include low cost, high efficiency and low toxicity. As such, CPE technique has been widely used for extracting trace metals and organic compounds coupled with atomic absorption spectrophotometry (AAS) [17–19], HPLC [20,21], etc. However, the use of surfactant-based procedure as a sample preconcentration step prior to capillary electrophoresis (CE) analysis has yet to not be fully explored. One problem associated with the introduction of a surfactant-rich phase into a bare fused-silica capillary is the surfactant adsorption onto the capillary

* Corresponding author. Tel.: +86 579 82282273; fax: +86 579 82282273.
E-mail address: cjr@zjnu.cn (J. Chen).

0039-9140/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.talanta.2011.04.009

wall that leads to a marked loss of efficiency and reproducibility [22].

It is well-known that CE has advantages, including greater peak resolutions, higher separation efficiency and shorter analytical time. Carabias-Martínez [23] first reported combined CPE with CE to detect triazine herbicides. In order to avoid the surfactant adsorption onto the capillary wall, non-aqueous separation buffer and dynamic coatings of the capillary tube were used. Later, it was reported the coupling of CPE with capillary electrochromatography (CEC) [24] and micellar elecrokinetic chromatography (MEKC) [25] as a tool to pre-concentrate and separate other organic compounds.

In the present work, we attempted to couple CPE with CE to analyze BPA, α-naphthol and β-naphthol. The optimized preconcentration and separation conditions were investigated in detail. The proposed methods were successfully applied to the analysis of BPA, α-naphthol, β-naphthol in river water samples.

2. Experimental

2.1. Reagents and solutions

Analytical grade BPA, α-naphthol and β-naphthol were purchased from ACROS ORGANICS (NJ, USA). The stock solutions of BPA, α-naphthol and β-naphthol with a concentration of 1 mg mL^{-1} were prepared in methanol. All solutions were kept at 4 °C in the dark.

The non-ionic surfactant Triton X-114 (Sigma-Aldrich, Steinheim, Germany) was used without any purification. A stock solution of Triton X-114 with a concentration of 50 g L^{-1} was prepared in distilled water. 50 mM sodium tetraborate ($Na_2B_4O_7{\cdot}10H_2O$, AR, Shanghai Reagent Factory, Shanghai, China) in 30% methanol (HPLC grade) used as CE buffer was freshly prepared daily. All the buffers were filtered through a 0.45 μm membrane filter and sonicated for 5 min to remove bubbles before the CE experiment. Purified water from a Milli-Q system was used throughout the experiments.

2.2. Apparatus and conditions

All CE experiments were performed with a Beckman P/ACE MDQ capillary electrophoresis system (Beckman Instruments, Fullerton, CA, USA) equipped with a diode array detector. The system was controlled by 32 Karat software and separation was performed at the following conditions: total length 60.2 cm, effective length 50 cm × 75 μm i.d., 375 μm o.d. fused-silica capillaries (Yongnian Optical Fiber Co. Ltd., Hebei, China); separation temperature of 25 °C and detection wavelength at 214 nm.

The pH of the electrolyte was measured by a PHS-3CT pH meter equipped with a glass-combined electrode. A centrifuge was used to accelerate the phase separation process. A thermostated water bath (Shanghai YIHENG Technical Co. Ltd., Shanghai, China) was used to maintain suitable temperatures for cloud point temperature experiments.

2.3. Procedures

2.3.1. Cloud point preconcentration procedure

For CPE, 200 μL 5.00% (m/v) Triton X-114 aqueous solution was added to 10 mL sample or standard solution and adjusted to pH 3.0. Then, the mixture solution was heated for 10 min in a thermostatic bath at 30 °C. Separation of the two phases was accelerated by centrifuging at 4000 rpm for 10 min. Upon cooling in an ice-bath, the surfactant-rich phase became viscous and was retained at the bottom of the tubes. The aqueous phases can be easily discarded by simply inverting the tubes. In order to reduce the surfactant-rich phase viscosity, 200 μL acetonitrile was added to the remaining surfactant-rich phase before CE separation.

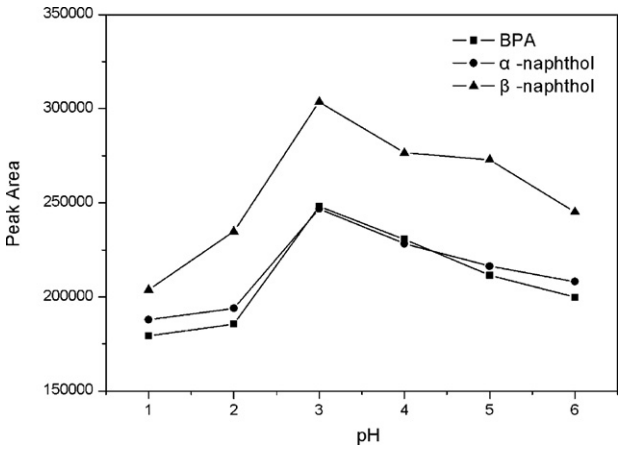

Fig. 1. Effect of pH on the extraction of BPA (10 mg L^{-1}), α-naphthol (5 mg L^{-1}), β-naphthol (5 mg L^{-1}). Capillary electrophoresis conditions: 50 mM sodium tetraborate buffer containing 30% (v/v) methanol (pH 9.5); voltage on separation was 25 kV; hydrodynamic injection at 0.5 psi, 5 s; UV detection 214 nm; capillary, 50 cm × 75 μm i.d., 375 μm o.d. CPE conditions: 0.10% (w/v) Triton X-114; cloud point temperature 30 °C.

2.3.2. Determination of analytes by CE

The capillary was treated prior to its first use by flushing in sequence with methanol for 5 min, distilled water for 2 min, 1.0 M NaOH for 5 min, distilled water for 2 min and running buffer for 10 min. The capillary was thereafter, equilibrated with 20 mM sodium tetraborate for 20 min. Routinely each day, the capillary was rinsed in a sequential order with 0.1 M NaOH, distilled water, running buffer for 5 min, 5 min and 10 min. To achieve high reproducibility of migration times and avoid solute adsorption, the capillary was washed between two runs with a rinse-cycle of methanol for 1 min, 1.0 M NaOH for 2 min, followed by distilled water for 2 min, and finally flushed with the buffer for 5 min. The samples were injected by applying a pressure of 0.5 psi at the anodic side for 5 s.

3. Results and discussion

3.1. Optimization of the preconcentration step

3.1.1. Effect of pH

As BPA and α-naphthol, β-naphthol are weakly acidic compounds (pK_a 9.73 [26], 9.30 [27], and 9.76 [28]), the pH of solution has great impact on their degree of ionization. A high pH can cause the ionization of compounds under investigation. The ionic form of analytes does not interact with the micellar aggregate as strongly as does its neutral form. As a result, smaller amount of analytes is extracted [29]. As such, the extraction of BPA, α-naphthol and β-naphthol was studied with the pH from 1.0 to 6.0. As shown in Fig. 1, the peak areas of BPA, α-naphthol and β-naphthol increased with pH increasing in the range of 1.0–3.0. However, the decrease of peak areas was observed, when pH was higher than 3.0. That due to lower pH value BPA and naphthols are neutral molecular form, they can be easily extracted into surfactant-rich phase. Hence, the optimum pH value of 3.0 was selected for the analysis.

3.1.2. Effect of Triton X-114 concentration on CPE

The effects of Triton X-114 concentration on sensitivity and extraction parameters were also examined in the range of 0.05–0.20% (m/v). With increasing of Triton X-114 concentration above 0.10% (m/v), the peak area decreased (refer to Fig. 2). Further increase in the concentration of Triton X-114 (higher than the optimum value) resulted in a decrease in the absorbance of the analyte. This is probably due to the potential adsorption of the excess

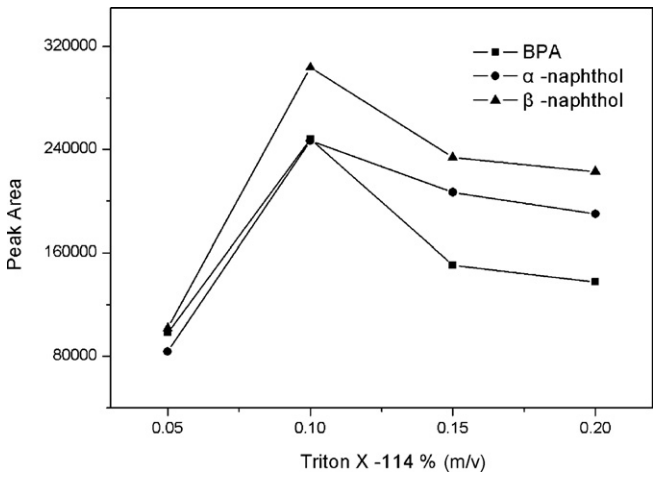

Fig. 2. Effect of surfactant concentration on the extraction of BPA (10 mg L^{-1}), α-naphthol (5 mg L^{-1}), β-naphthol (5 mg L^{-1}). CPE conditions: pH 3; cloud point temperature 30 °C. CE conditions as in Fig. 1.

surfactant onto the capillary wall. In order to achieve higher extraction efficiency of the target analyte, enrichment factor of the system and satisfactory reproducibility, 0.10% (m/v) Triton X-114 was selected for the following experiments.

3.1.3. Effects of equilibration temperature and time

Both the equilibration temperature and time play important roles in the outcome of CPE performance. It is desirable to employ the shortest equilibration time, lowest temperature and quantitative extraction during the experiment. Hence, equilibration temperature and time were optimized to enable complete extraction and make phase separation easily. The study on the effect of equilibration temperature was performed within the temperature range of 25–50 °C. In Fig. 3, it can be seen that an optimal temperature of 30 °C was found for the extraction of quantitative analysis.

The dependence of extraction efficiency on equilibration time was investigated from 10 to 25 min. The results showed that 10 min was sufficient to achieve complete phase separation. Therefore, an equilibration time of 10 min was employed for the following experiments.

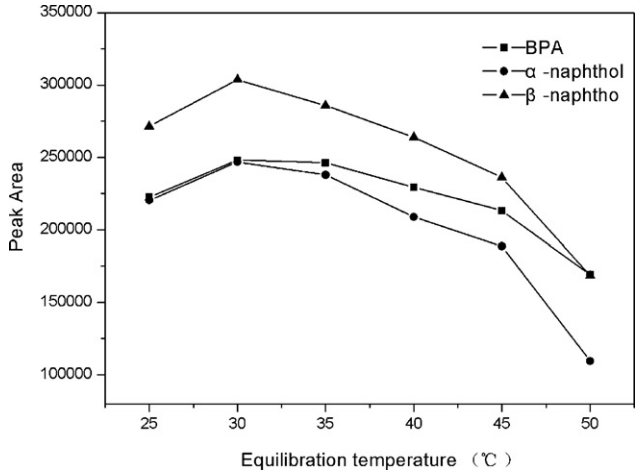

Fig. 3. Effect of equilibration temperature on the extraction of BPA (10 mg L^{-1}), α-naphthol (5 mg L^{-1}), β-naphthol (5 mg L^{-1}). CPE conditions: 0.10% (w/v) Triton X-114; pH 3. CE conditions as in Fig. 1.

3.1.4. Effect of dilution solvent

The surfactant-rich phase obtained after CPE was too viscous for direct injection into the capillary electrophoresis system. It was apparent that suitable dilution should be made before the CE experiment. The use of different solvents (methanol and acetonitrile) for the surfactant-rich phase was also attempted in order to dilute adequately and satisfactorily for CE sample introducing. The results showed that high viscosity of the surfactant-rich phase was markedly decreased and analytes baseline separation was achieved using 200 μL acetonitrile. Therefore, the surfactant-rich phase was diluted with 200 μL acetonitrile before introducing it into the CE sample vial.

3.2. Optimization of the separation conditions

In order to propose a specific and sensitive way to analyze CPE-preconcentrated samples containing BPA, α-naphthol and β-naphthol by capillary zone electrophoresis, several parameters that affect the CE separation were studied as follows.

3.2.1. Effect of BGE composition and concentration

The addition of an organic modifier such as methanol or acetonitrile to the running electrolyte can effectively improve separation selectivity. This is achieved via the alteration of viscosity and the electro-osmotic flow (EOF) reduction of the system [30]. In order to discover an appropriate background electrolyte (BGE) for the separation of the analytes, 50 mM sodium tetraborate containing 10–40% (v/v) methanol or acetonitrile was tested in the study. The results however, showed that no improvement on the separation efficiency and baseline fluctuation was observed when acetonitrile was used as the modifier. The current appeared to level off when 30% (v/v) methanol was added.

In addition, the effect of sodium tetraborate concentration on separation was investigated in the range of 20–70 mM in 30% (v/v) methanol. It was found that when sodium tetraborate concentration increased, the separation efficiency and migration time also increased. A stable baseline was obtained with 50 mM sodium tetraborate in 30% (v/v) methanol. Hence, 50 mM sodium tetraborate in 30% (v/v) methanol was chosen as the running buffer.

3.2.2. Effect of BGE pH value

The pH value of running buffer has been recognized as one of the most important parameters for CE separation. It can influence mobility of analyte by adjusting EOF velocity and the ionic charge of analyte molecules [31]. The effect of the running buffer pH was investigated within range of 7.0–10.0 at a buffer concentration of 50 mM. The baseline separation could be achieved at pH 9.5 and above. Higher pH can result in peak tailing and the increase in migration time. With respect to all the factors, the optimum pH value of 9.5 was therefore applied to obtain better peak shapes and shorter analytical time.

3.2.3. Effect of applied voltage on separation

The effect of applied voltage on separation was investigated in the range of 15–30 kV. Results showed that baseline separation could be achieved in the tested voltage range. With increasing applied voltage, the resolution efficiency increased with a shorter analytical time. However, a higher separation voltage causes detrimental Joule effect that can lead to the peak overlaps. Considering about all factors, a voltage of 25 kV was therefore applied.

Based on all the discussed factors, optimum performance was obtained with a running buffer of 50 mM sodium tetraborate in 30% (v/v) methanol (pH 9.5), and an applied voltage of 25 kV.

Table 1
Results of linear range, regression data and concentration limits of detection for the analytes.

Organic compounds	Concentration range (mg L^{-1})	Regression equation	R^2	C_{LOD} ($S/N = 3$) (μg L^{-1})	C_{LOQ} ($S/N = 10$) (μg L^{-1})
BPA	0.2–10	$23960x + 780$	0.9996	0.50	1.67
α-Naphthol	0.1–5	$49620x - 270$	0.9999	0.24	0.80
β-Naphthol	0.1–5	$61480x - 100$	0.9999	0.20	0.67

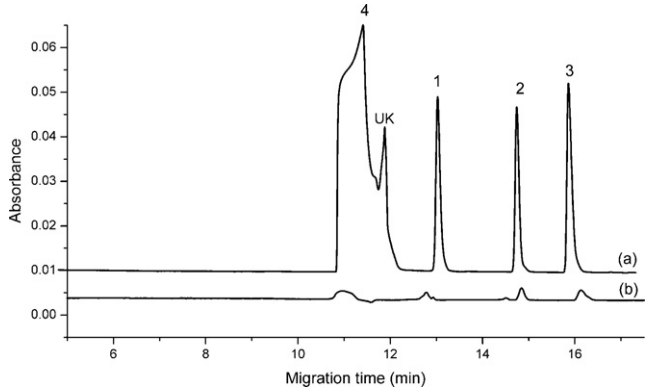

Fig. 4. Electropherograms of the standard solution obtained by (a) CPE-CE analysis and (b) direct CE (1 BPA 10 mg L^{-1}; 2 α-naphthol 5 mg L^{-1}; 3 β-naphthol 5 mg L^{-1}; 4 Triton X-114). CPE conditions: 0.10% (w/v) Triton X-114; pH 3; cloud point temperature 30 °C. CE conditions as in Fig. 1.

3.3. Calibration, precision and detection limit

To evaluate the quantitative applicability of the method by establishing the calibration curves. The three analytes in the different concentration were prepared by CPE (stated in Section 2.3.1) and then analyzed in CE under optimum experimental conditions. Linear relationships between the peak area and the concentration of BPA, α-naphthol and β-naphthol were investigated. Refer to Table 1 for the calibration parameters and the detection limits. The BPA levels considered under this study were also compared with other methods. They showed lower LOQ compared with SPME-HPLC (3.8 μg/L) [32] and SPE-HPLC-UV (30 μg/L) [33]. Although CPE-CE is not a sensitive determination method like HPLC–MS [10,11] and GC–MS [12], it is worthy to note that the method under this study is more simple, rapid, inexpensive, greener and easier to use.

The standard electropherogram of BPA, α-naphthol and β-naphthol under the optimal experimental conditions are shown in Fig. 4. A base-line separation for the analytes could be achieved within 17 min. In this study, the inter-day precisions of migration time and peak area were less than 0.38% and 5.66% for BPA, α-naphthol, β-naphthol. The preconcentration factor (calculated as the ratio of the volume of preconcentration samples to the volume of the surfactant-rich phase) was 50-folds. The electropherograms of standard samples obtained by CPE-CE and direct CE analysis under optimum conditions are shown in Fig. 4.

3.4. Determination of BPA, α-naphthol and β-naphthol in water samples

In order to test the reliability of the proposed methodology suitable for assaying BPA, α-naphthol and β-naphthol, the proposed method was applied to determine their concentrations in river water (Wujiang, Jinhua, China). 10 mL of the sample solution was treated using cloud point preconcentration procedure, and then detected by CE at optimum conditions. However, when the methods were applied to the real sample (river water), no signal response was detected. This may possibly be due to the reason that the concentration of analytes in the real samples was below the LODs of the present methods. Thus, known quantities of analytes were added to the aliquots of river water sample, and the recovery experiments were performed to confirm the validity of the proposed method. The recoveries for the analytes were in the range of 92.4–104.4% and demonstrated that the river waters matrices had little effect on the CPE, and the results are listed in Table 2.

Table 2
Determination of organic compounds in water samples ($n = 3$).

Samples	Added (μg L^{-1})	Measured (μg L^{-1})	Recovery (%)
BPA	0	ND[a]	
	200	198.8	99.40
	400	417.7	104.4
	800	771.7	97.14
α-Naphthol	0	ND[a]	
	100	102.5	102.5
	200	206.0	103.0
	400	405.3	101.3
β-Naphthol	0	ND[a]	
	100	100.7	100.7
	200	197.6	98.79
	400	369.7	92.43

[a] Not Detected.

4. Conclusions

The present study is the first of its kind to describe the coupling of CPE with CE technique for the preconcentration and analysis of BPA, α-naphthol and β-naphthol. This method offers various advantages, including efficacy, safety, rapid analysis and low cost. In addition, the surfactant-rich phase diluted with 200 μL acetonitrile can be directly introduced into CE instrument and detection can easily be performed. With Triton X-114 as surfactant for preconcentration, high extraction efficiency and recoveries could be obtained. The proposed method was applied to detect the compounds of BPA, α-naphthol and β-naphthol in river water at low level quantities with satisfactory results.

Acknowledgement

Financial support from Chinese National Natural Science Foundation (No. 90406016) is gratefully acknowledged.

References

[1] S. Stephen, Toxicology 205 (2004) 3–10.
[2] M. Alaee, P. Arias, A. Sjödin, Å. Bergman, Environ. Int. 29 (2003) 683–689.
[3] X. Wang, H. Zeng, Y. Wei, J. Lin, Sens. Actuators B: Chem. 114 (2006) 565–572.
[4] L.N. Vandenberg, R. Hauser, M. Marcus, N. Olea, Reprod. Toxicol. 24 (2007) 139–177.
[5] V.E. Forbes, H. Selck, A. Palmqvist, J. Aufderheide, R. Warbritton, N. Pounds, R. Thompson, N. Hoeven, N. Caspers, Ecotoxicol. Environ. Safe. 66 (2007) 319–325.
[6] H.S. Shin, D.M. Lim, D.H. Lee, K.H. Kang, Bioresour. Technol. 80 (2001) 29–36.
[7] S. Ortega-Algar, N. Ramos-Martos, A. Molina-Díaz, Talanta 60 (2003) 313–323.
[8] S. Zang, B. Lian, J. Hazard. Mater. 166 (2009) 33–38.
[9] W. Zhang, C. Hong, B. Pan, Z. Xu, Q. Zhang, L. Lu, J. Hazard. Mater. 158 (2008) 293–299.
[10] M. Rezaee, Y. Yamini, S. Shariati, A. Esrafili, M. Shamsipurc, J. Chromatogr. A 1216 (2009) 1511–1514.
[11] S.G. Chu, G.D. Haffner, R.J. Letcher, J. Chromatogr. A 1097 (2005) 25–32.
[12] W. Yan, Y. Li, L.X. Zhao, J.M. Lin, J. Chromatogr. A 1216 (2009) 7539–7545.
[13] Y. Zhang, H. Zhuang, Electrochim. Acta 54 (2009) 7364–7369.
[14] N.C. Maragou, E.N. Lampi, N.S. Thomaidis, M.A. Koupparis, J. Chromatogr. A 1129 (2006) 165–173.

[15] J. Salafranca, R. Batlle, C. Nerín, J. Chromatogr. A 864 (1999) 137–144.
[16] W. Wen, J. Miao, W. Yu, Chin. J. Anal. Lab. 28 (2009) 107–109.
[17] J. Chen, S. Xiao, X. Wu, K. Fang, W. Liu, Talanta 67 (2005) 992–996.
[18] J. Chen, K. Teo, Anal. Chim. Acta 450 (2001) 215–222.
[19] X. Jiang, S. Wen, G. Xiang, J. Hazard. Mater. 175 (2010) 146–150.
[20] Z. Zhou, J. Chen, D. Zhao, M. Yang, J. Agric. Food Chem. 57 (2009) 8722–8727.
[21] C.M. Santana, Z.S. Ferrera, J.J.S. Rodríguez, Analyst 127 (2002) 1031–1037.
[22] S. Xie, M.C. Paau, C.F. Li, D. Xiao, M.M.F. Choi, J. Chromatogr. A 1217 (2010) 2306–2317.
[23] R. Carabias-Martínez, E. Rodríguez-Gonzalo, J. Domínguez-Alvarez, J. Hernández-Méndez, Anal. Chem. 71 (1999) 2468–2474.
[24] P.W. Stege, L.L. Sombra, G.A. Messina, L.D. Martinez, M.M.F. Silva, Anal. Biochem. 394 (2009) 567–573.
[25] Y. Wu, Y. Jiang, T. Xiao, H. Zhang, J. Sep. Sci. 31 (2008) 865–871.
[26] H. Sambe, K. Hoshina, K. Hosoya, J. Haginaka, J. Chromatogr. A 1134 (2006) 16–23.
[27] W. Wall, J. Li, Z.E. Rassi, J. Sep. Sci. 25 (2002) 1231–1244.
[28] C. He, J. Huang, C. Yan, J. Liu, L. Deng, K. Huang, J. Hazard. Mater. 180 (2010) 634–639.
[29] S. Akita, H. Takeuchi, Sep. Sci. Technol. 30 (1995) 833–846.
[30] C. Corradini, F. Bianchi, D. Matteuzzi, A. Amoretti, J. Chromatogr. A 1054 (2004) 165–173.
[31] W. Wang, C. Li, Y. Li, Z. Hu, X. Chen, J. Chromatogr. A 1102 (2006) 273–279.
[32] C. Nerín, M.R. Philo, J. Salafranca, L. Castle, J. Chromatogr. A 963 (2002) 375–380.
[33] K. Inoue, K. Kato, Y. Yoshimura, T. Makino, H. Nakazawa, J. Chromatogr. A 749 (2000) 17–23.