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Electrically assisted solid-phase microextraction combined with liquid chromatography–mass spectrometry for determination of parathion in water

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ABSTRACT

A novel method for electrically assisted microextraction coupled to liquid chromatography–mass spectrometry was evaluated for determination of trace levels of parathion in water. A pencil lead electrode was used in a di-electrode system to extract parathion onto the electrode surface with a reductive potential applied. The optimum extraction conditions were found to be a potential of −600 mV for 60 s in pH 2 phosphate buffer solution. The parathion was desorbed statically for 1 min and dynamically for 3 min in the commercial SPME–HPLC desorption chamber, then analyzed with LC–APCI–MS/MS. The detection limit (LOD) for parathion in water was found to be 0.3 ng/mL. The proposed technique was demonstrated to be fast, sensitive and not require a solvent sample pretreatment.

1. Introduction

Most pesticides spread in agricultural applications cause environmental contamination of water, air and soil. Organophosphorous pesticides have been used widely in animal husbandry, crop protection and elimination of ectoparasites. Parathion is one of the most important organophosphorous pesticide compounds (OPs). The structure of parathion is shown in Fig. 1. It consists a thiophosphoric moiety linked to a nitrobenzene group. Its toxicity is primarily associated with inhibition of acetylcholinesterase (AChE) activity. It is absorbed quickly through the skin and eyes [1,2]. Therefore, monitoring traces of parathion in water is important [3].

Various analytical techniques have been used for determination of parathion in the environment, mainly employing chromatographic approaches, including gas chromatography–mass spectrometry (GC–MS) [4–8], liquid chromatography–mass spectrometry (LC–MS) [9,10], ion-mobility spectrometry coupled with mass spectrometer (IM-MS) [11] and capillary electrophoresis [12]. Electrochemical detection methods also are suitable for analysis because of desirable features of electrochemistry [13–17]. Although gas chromatographic methods frequently were applied for analysis of parathion, liquid chromatography often is preferred because of decreased restrictions on volatility.

Sample pretreatment is an important part of the proposed method. Various sample techniques were used to accurately determine parathion at trace levels in complicated matrices. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are generally used in analysis of parathion in water samples [18–21]. Because many organic solvents are required, this represents a threat to the environment and technician health in the laboratory. Solid-phase microextraction (SPME) has recently become popular because of the reduction in solvent use and exposure. Solid-phase microextraction (SPME), developed by Pawliszyn and colleagues in 1989 [22], was widely used for analytical toxicology [23], food [24–26] and environment [27] analysis. The detection limit of SPME can reach the ng per L^{-1} level. This technique is based on the distribution of analyte between the extracting phase and the matrix. SPME has advantages of simplicity, ease of use and concentration. New fibers of SPME techniques have been developed, such as different material of fiber (e.g. pencil lead) [28–32], surface adsorbent modification [33–36], electrochemically-controlled solid-phase microextraction (EC-SPME) [37–39]. An important aim of these improvements was to increase the efficiency of extraction and to improve the selectivity of SPME. However, some drawbacks have included fiber fragility, short fiber life-time, and a more expensive and longer equilibration time.

The purpose of this study is to develop electrically assisted solid-phase microextraction combined with LC–APCI–MS/MS for determination of parathion in environmental water. The main idea of this project was to focus on utilizing electrochemistry as a concentration approach. The pencil lead played two roles: an extraction fiber and a cathode. Pencil lead is a porous material that can provide very large surface area, enabling the electrochemical reac-

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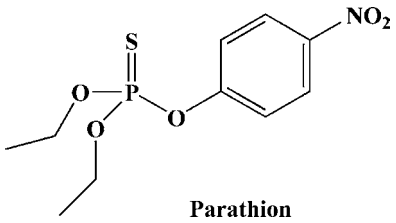

Fig. 1. The chemical structure of parathion.

tion. The preconcentration of parathion from the matrix occurred when a suitable reductive potential was applied to the electrode. The optimal parameters affecting extraction efficiency, including extraction potential, adsorption time, pH value and the stirring rate were studied. The performance of electrically assisted-SPME-LC–APCI–MS/MS to analyze parathion in water samples also was evaluated.

2. Experimental

2.1. Chemicals and reagents

The parathion used in this experiment was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The organic solvents and hydrochloride (HCl) were obtained from Merck (Darmstadt, Germany). All chemicals used in this study were analytical reagent or HPLC grade. The water was purified in the laboratory (>18 MΩ) using RiOs^{TM} 3 Water Purification Systems from Millipore Co. (Bollerica, MA, USA). The stock solution of parathion was prepared in methanol and stored at 4 °C in a refrigerator. The phosphate buffer solution consisted of 10 mM disodium hydrogen phosphate (Na_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4). The pH values of the phosphate buffer solutions were adjusted by altering the ratio of 10 mM Na_2HPO_4 and KH_2PO_4 solution.

2.2. Analytical conditions

The chromatographic system used was a Dynamax ProStar 210 liquid chromatograph (Thermo Finnigan, San Jose, CA, USA), employing two LC pumps. The parathion was separated on a ZORBAX 80 Å Extend-C18 LC column (15 cm × 2.1 mm, 5 μm) (Agilient Technologies, Palo Alto, CA, USA). Mobile phases A and B were water solution with 0.1% acetic acid and methanol with 0.1% acetic acid, respectively. The LC program was the isocratic elution at 90% of solvent B for 3 min and the flow rate of mobile phase was 500 μL/min.

A Varian 1200L triple-quadrupole LC/MS (Varian, Walnut Creek, CA, USA), equipped with an APCI source was used for the determination of parathion. The optimum voltages were found by tuning with an automated procedure that maximized the signal for the ions of parathion. The instrument conditions were described as follows: vaporizer temperature, 550 °C, drying gas temperature, 350 °C, drying gas pressure, 33 psi, nebulizer gas pressure, 30 psi, auxiliary gas pressure, 1.7 psi, shield voltage 450 V and corona current 3 μA. For quantitation, selected reaction monitoring (SRM) was used to increase the sensitivity and selectivity for trace parathion. During the SRM analysis mode, mass peak width was 2.0 Th for Q1 and 1.0 Th for Q3. The collision gas was argon at a pressure of 2.0 mtorr.

2.3. Extraction procedure

The extraction device shown in Fig. 2 was constructed in the authors laboratory. A pencil lead HB (5.5 cm × 0.3 mm) (Pilot Co., Tokyo, Japan) was purchased from the commercial market. It was

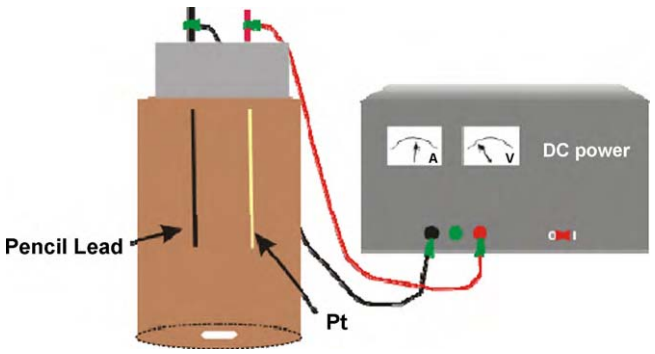

Fig. 2. Schematic of electrode microextraction device.

used as a cathode while platinum was used as an anode in the two electrode system. Both electrodes were fixed by the septum at a distance of 1 cm. The DC power supply unit was purchased from SANCO Electronics Co., Ltd. (Ningbo, Zhejiang, China) and used to adjust the potential. Cyclic voltammetric (CV) measurement of parathion was performed with a BAS Epsilon electrochemistry workstation (Bioanalytical Systems, West Lafayette, IN, USA). The three electrode system used a pencil lead as the working electrode, Ag/AgCl as a reference electrode and platinum as an auxiliary electrode. Before electrochemical analysis, deoxygenation was performed by purging with high-purity nitrogen (>99%) for 10 min.

The extraction procedure was performed as follows: 5 mL of a water sample containing parathion adjusted to pH 2 was added to 5 mL brown glass vial. A PTFE/silicone septum was used to hold the pencil lead and platinum electrode. Before performing experiment, the electrode was inserted into aqueous phosphate buffer solution of pH 2 until the current was stable. Then two electrodes were transferred to the solution containing parathion. A DC potential was applied on the electrodes at −600 mV for 60 s. When the extraction was complete, the pencil lead was transferred to the SPME/HPLC desorption chamber (Supelco, Bellefonte, PA, USA). The compound was desorbed with 200 μL methanol in static desorption mode for 1 min, in dynamic mode for 3 min with mobile phase and then detected by LC–APCI/MS/MS.

2.4. Water sample analysis

River water and ground water were collected from Taichung city, in central Taiwan. Before storing at 4 °C in the refrigerator, the samples were acidified with 0.1N HCl and the pH was adjusted to 2. Prior to analysis, the water sample was filtered with a 0.22 μm syringe filter (Millipore, Billerica, MA, USA). 5 mL samples were taken with the home-made extraction system, then the analyte was extracted under the optimum conditions of electrode microextraction. Finally, the extract was analyzed by LC–APCI–MS/MS.

3. Results and discussion

3.1. Electrochemical behavior of parathion on the electrode and its mass spectrum

The electrochemical characteristics of parathion at the pencil lead working electrode were studied first. The continuous cyclic voltammetric (CV) response of 1 μg/mL parathion on the pencil lead electrode in pH 2.0 phosphate buffer was measured at a scan rate of 100 mV/s over the range of +0.6 to −0.6 V. The cyclic voltammogram is shown in Fig. 3. The results indicate that the first cathodic peak at −400 mV in curve A is due to four-electron reduction of parathion with irreversible transformation from the φ-NO_2 into φ-NHOH. In a preliminary experiment, the pencil lead was held at a

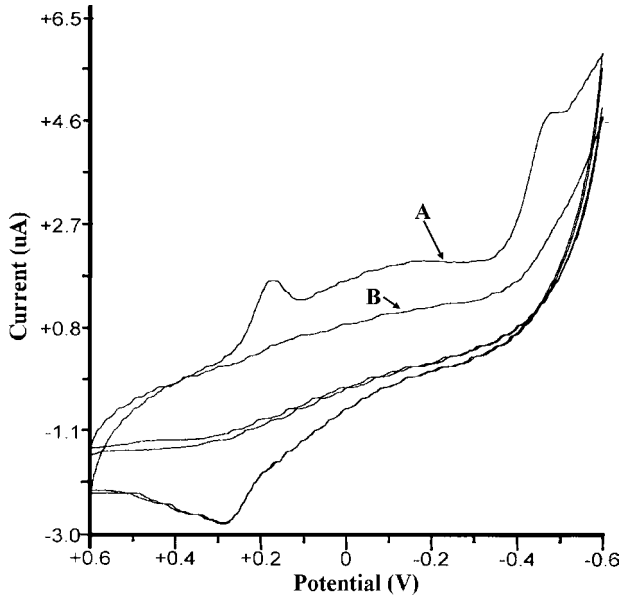

Fig. 3. Cyclic voltammetric response of 1 μg/mL parathion (A) and blank (B) at pencil lead electrode in pH 2.0 phosphate buffer solution. The scan rate was 100 mV s^{-1} and switching potentials +0.6 and −0.6 V.

DC potential of −400 mV for 1 min and then the extract adsorbed on the electrode was desorbed using 1 mL of methanol for a few minutes. The solution was analyzed by LC–APCI–MS. The mass range was setting at *m*/*z* 100–300. Total ion extracted ion chromatograms using LC–APCI–MS analysis are shown in Fig. 4. The ion extracted chromatogram and demonstrated that parathion, *m*/*z* 292 and the reductive product of parathion, *m*/*z* 278 were adsorbed on the surface of the pencil lead. The different types of pencil lead were evaluated including HB-, B- and 2B-type. The results were shown in Fig. 5 and indicated that the signal of parathion extracted by HB-type of pencil lead with electrochemical-assisted is higher than that extracted by using B- and 2B-type of pencil lead. Therefore, the HB-type pencil lead was chosen as the electrode. In the MS/MS experiment, the product ion spectrum of the protonated

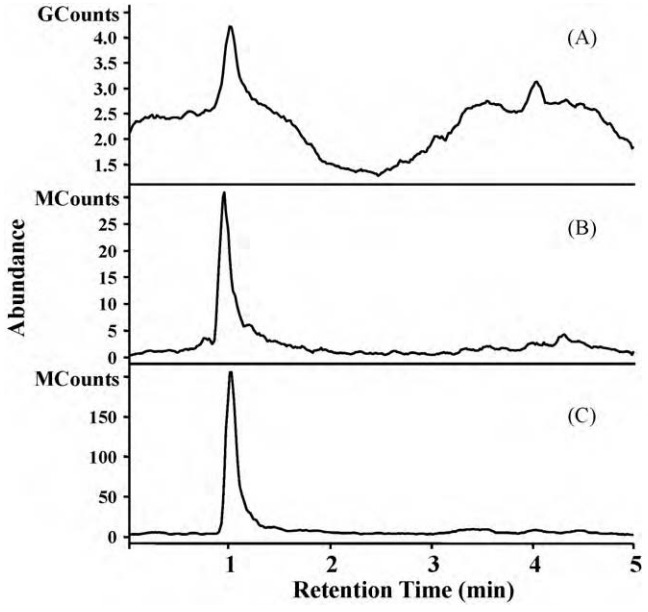

Fig. 4. Total ion chromatogram of parathion using LC–APCI–MS after electrode extraction. (A) TIC; (B) φ-NO_2, $[M+H]^+$ *m*/*z* 292; (C) φ-NHON, $[M+H]^+$ *m*/*z* 278.

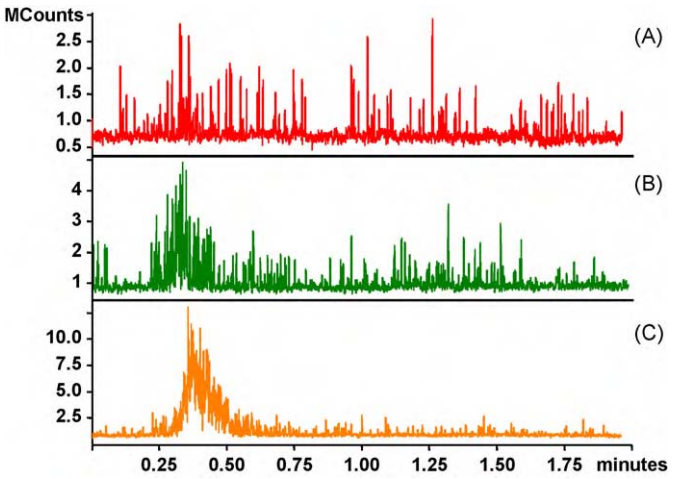

Fig. 5. Mass ion chromatogram of 50 ng mL^{-1} of parathion on the different type of pencil lead produced by electrically assisted-SPME-LC–MS/MS. (A) 2B-; (B) B-; (C) HB-type.

molecule $[M+H]^+$, *m*/*z* 292 of parathion (φ-NO_2) was produced by LC–APCI–MS/MS. The most abundant product ion $[M+H-2C_2H_4]^+$, *m*/*z* 236 was the base peak and selected as the quantitative ion. *m*/*z* 264 $[M+H-C_2H_4]^+$ of product ion was as qualitative ion.

3.2. Electrically assisted solid-phase microextraction conditions

3.2.1. Effect of pH

For conventional SPME, the pH of the solution was adjusted to make the neutral form of analytes, which were adsorbed on the SPME fiber. In electrode extraction, the pH of the solution also is a critical factor affecting the electrochemical characteristics of parathion and the properties of the pencil lead electrode. The variations of the potential and peak area of analytes with the pH of solution were studied. The phosphate buffer solution was used to adjust the pH values of solution from 2.0 to 6.0. The effect of pH values on peak area of parathion using electrode extraction combined with LC–APCI–MS/MS is shown in Fig. S1. The peak area of parathion increased with decreasing pH from 6.0 to 2.0. This demonstrates that protonation enhanced the ability of parathion to be adsorbed on the electrode.

3.2.2. Effect of extraction potential and extraction time

The nitro group of parathion has good electrochemical characteristics. When reductive potential was applied at the electrode, a portion of the parathion was adsorbed on the surface of the pencil lead cathode. The potential effect on the peak area of parathion was studied from 0 to −1000 mV (Fig. S2). When the SPME fiber is immersed in the solution at 0 mV, parathion is adsorbed without any applied potential. As the negative potential was varied from 0 to −600 mV, extraction efficiency increased quite significantly. The analyte is adsorbed into a small volume concentrated on the surface of cathode. More negative potentials did not improve the peak area of parathion (i.e., extraction efficiency). This indicated a good film formation at a potential of −600 mV.

The compound concentration on the electrode is a time-dependent mass-transfer process. The extraction time was varied from 10 to 80 s and fresh samples were prepared for each extraction in an effort to find the optimum adsorption time. The peak area increased with increasing extraction time and reached to a maximum at 60 s (Fig. S3). This shows that the surface of the electrode was saturated and the maximum possible amount of parathion was extracted. Hence, the optimized electrode extraction setting of −600 mV for 60 s was used in further experiments.

Table 1
Analytical characteristics of electrically assisted-SPME-LC/MS/MS method for determination of parathion in water samples.

Compound	Linear range (ng/mL)	Linear equation	R^2	LOD (ng/mL)	LOQ (ng/mL)	R.S.D (%) (n = 4)
Parathion	10–1000	$y = 6411.5x - 241{,}172$	0.9999	0.3	1.0	1.0

Table 2
The results of parathion in various samples, recoveries and precisions produced by proposed method.

Sample	Concentration ($ng\,mL^{-1}$)	Spiked concentration ($ng\,mL^{-1}$)			
		10		50	
		Recovery[a,b] (%)	R.S.D.[b] (%)	Recovery (%)	R.S.D. (%)
Farm water	N.D.[c]	87.0	11.4	90.3	9.1
Ground water	N.D.	71.6	13.1	79.2	3.9
River water	N.D.	115.7	7.7	62.5	5.2
Tap water	N.D.	102.4	9.1	91.6	9.4

[a] Recovery (%) = $C_{spiked} \times 100/C_{std}$.
[b] n = 3.
[c] Not detected.

3.2.3. Effect of stir rate

The electrical double layer (EDL) may influence the efficiency of the mass transfer between the solution and the electrode during extraction. The optimum stirring rate is very important in electrode extraction, because diffusion through bulk fluid is slow. The stirring rate was varied from 630 to 1086 rpm in this study and the result is shown in Fig. S4. The curve of peak area increased sharply with the rate of stirring. This result shows that the mass-transfer efficiency was enhanced with increasing the stirring rate. When the rotation speed of a magnet was too fast, the adsorption process was suppressed, probably by the shear stress of whirlpool. The extraction efficiency was decreased at stirring rate over 744 rpm. Hence the optimum stirring rate was determined to be 744 rpm.

3.2.4. Matrix effect

To study matrix effects, the groundwater samples were spiked with 500 ng/mL standard parathion solution, and then diluted with pH 2 phosphate buffer solution to form a series of V_{sample}/V_{buffer} concentration ratio of 1/4, 2/3, 1/1, 3/2, 4/1. The total sample volume was kept constant. The results are shown in Fig. S5 with the greatest extraction efficiency observed when 4 mL of sample solution was combined with 1 mL of pH 2 of buffer solution. Comparing with the acidified samples (with no buffer solution dilution), the peak area of the acidified solution is higher than any diluted samples with pH 2 phosphate buffer. This result suggests that matrix effects in this study had no clear influence at lower pH.

3.3. Method validation and real samples analysis

The linearity, detection limit and precision were used to evaluate the performance of electrically assisted solid-phase microextraction-LC–MS/MS under the optimum conditions. The results are listed in Table 1. The linearity of electrode extraction was calculated by extracting spiked parathion samples over the concentration range of 10–1000 ng/mL. The correlation coefficient (R^2) of the linearity was 0.9999. The limit of detection and quantitation for electrically assisted solid-phase microextraction-LC–MS/MS was 0.3 and 1.0 ng/mL respectively, based on the lowest point of linearity with 3 and 10 standard deviation to the slope of linearity. According to the EU's drinking water standards (Council Directive 98/83/EC), the maximum acceptable concentration of total pesticides in drinking water is 0.5 and 0.1 $\mu g\,L^{-1}$ for the one kind of pesticide [40]. In the guideline of World Health Organization (WHO), there is no specification for the residue of pesticide in drinking water. The effectiveness of the proposed method in determining parathion in real samples was tested by analyzing river (South, Taichung City), tap (South, Taichung City), farm water (Dali, Taichung County) and ground water (South, Taichung City) samples. None of them was detected by electrically assisted solid-phase microextraction combined with liquid chromatography–mass spectrometry. Triplicate measurements of spiking 2-level concentrations of parathion in different water samples were used in recovery evaluation. The results are shown in Table 2. Recoveries of parathion in water samples were calculated from the measured concentration divided by the spiked concentration, and the recoveries varied from 62.5% to 91.6% with R.S.D. from 3.9% to 9.4%. The result demonstrates the suitability of electrically assisted-SPME-LC–MS/MS for analyzing trace parathion in water samples.

3.4. Comparison of electrically assisted-SPME with different extraction method

Comparison of the presented method with various extraction, such as solid-phase microextraction (SPME) [41], solid-phase extraction (SPE) [42], micellar extraction (cloudy extraction) [43], single drop microextraction (SDME) [44], for the analysis of parathion in water samples are summarized in Table 3. The comparison of the results shows that extraction time in electrically assisted-SPME is very short and the equilibrium of extraction time

Table 3
Comparison of the proposed method with different methods for determination of parathion.

Extraction method	Extraction time (min)	LOD	R.S.D. (%)	Recovery (%)	Ref.
SPME	30	0.049 ($\mu g\,L^{-1}$)	4.9	99.2	[41]
SPE	–	130 ($ng\,L^{-1}$)	4.0	93.8–104.5	[42]
Micellar extraction	15	2.0 ($ng\,mL^{-1}$)	1.6	80.4–84.5	[43]
SDME	20	0.21 ($ng\,mL^{-1}$)	3.5	91.7–96.9	[44]
LPME	20	0.02 ($\mu g\,L^{-1}$)	4.4	97–104	[45]
Presented method	1	0.3 ($ng\,mL^{-1}$)	1.0	75.8	–

is achieved at 1 min. The R.S.D. value is quite low for electrically assisted-SPME because of quick achievement of equilibrium. Therefore the proposed method, electrically assisted-SPME combined with LC–MS for determination of parathion in water sample, is a very simple, rapid without any special approaches.

4. Conclusions

This project is the first application of electrically assisted solid-phase microextraction coupled to LC–MS/MS for detection of electrochemically active compounds. A method based on electrically assisted solid-phase microextraction (electrically assisted-SPME) combined with liquid–chromatography tandem mass spectrometry (LC/MS/MS) for determining trace amount of parathion in water samples was demonstrated. Inexpensive pencil lead (HB-type) served as an extraction probe and as a cathode in this project. At reductive potential, both neutral molecules and reduced derivatives were adsorbed on the surface of the pencil lead electrodes. The feasibility of electrically assisted-SPME-LC/MS/MS was evaluated for determination of the trace amount of parathion in water samples. The results show that equilibrium is reached with an extraction time of only 60 s. The extraction time is faster than the conventional SPME. The method provides a widely linear range (10–1000 ng/mL) and good sensitivity with low limit of detection at 0.3 ng/mL. Electrically assisted solid-phase microextraction is a cheaper, more sensitive, and fast pretreatment method for trace compounds determination.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.05.053.

References

[1] F.R. Chuang, S.W. Jang, J.L. Lin, Am. J. Emerg. Med. 14 (1996) 451–453.
[2] N.H. Knaak, Rev. Environ. Contam. Toxicol. 163 (2000) 29–111.
[3] D. Barceló, Analyst 116 (1991) 681–689.
[4] J. Gao, L. Liu, X. Liu, H. Zhou, J. Lu, S. Huang, Z. Wang, Bull. Environ. Contam. Toxicol. 82 (2009) 223–229.
[5] P. Pugliese, J.C. Molto, P. Damiani, R. Marin, L. Cossignani, J. Manes, J. Chromatogr. A 1050 (2004) 185–191.
[6] M. Schellin, B. Hauser, P. Popp, J. Chromatogr. A 1040 (2004) 251–258.
[7] C.G. Zambonin, M. Quinto, N. De Vietro, F. Palmisano, Food Chem. 86 (2004) 269–274.
[8] M.P. García de Llasera, M.L. Reyes-Reyes, Food Chem. 114 (2009) 1510–1516.
[9] A.R. Fernández-Alba, J.F. García-Reyes, Trends Anal. Chem. 27 (2008) 973–990.
[10] Y. Picó, C. Blasco, G. Font, Mass Spectrom. Rev. 23 (2004) 45–85.
[11] M. Nousiainen, K. Perakorpi, M. Sillanpaa, Talanta 72 (2007) 984–990.
[12] J. Hernández-Borges, S. Frías-García, A. Cifuentes, M.A. Rodríguez-Delgado, J. Sep. Sci. 27 (2004) 947–963.
[13] M. Sbaï, H. Essis-Tome, U. Gombert, T. Breton, M. Pontié, Sens. Actuator B: Chem. 124 (2007) 368–375.
[14] G. Liu, Y. Lin, Electrochem. Commun. 7 (2005) 339–343.
[15] C. Li, C. Wang, B. Guan, Y. Zhang, S. Hu, Sens. Actuator B: Chem. 107 (2005) 411–417.
[16] S.V. Dzyadevych, A.P. Soldatkin, V.N. Arkhypova, A.V. El'skaya, J.-M. Chovelon, C.A. Georgiou, C. Martelet, N. Jaffrezic-Renault, Sens. Actuator B: Chem. 105 (2005) 81–87.
[17] R.P. Deo, J. Wang, I. Block, A. Mulchandani, K.A. Joshi, M. Trojanowicz, F. Scholz, W. Chen, Y. Lin, Anal. Chim. Acta 530 (2005) 185–189.
[18] F. Hernández, J.V. Sancho, O. Pozo, A. Lara, E. Pitarch, J. Chromatogr. A 939 (2001) 1–11.
[19] F.E. Ahmed, Trends Anal. Chem. 20 (2001) 649–661.
[20] S. Wang, P. Zhao, G. Min, G. Fang, J. Chromatogr. A 1165 (2007) 166–171.
[21] J. Liu, L. Wang, L. Zheng, X. Wang, F.S.C. Lee, J. Chromatogr. A 1137 (2006) 180–187.
[22] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2148.
[23] F. Pragst, Anal. Bioanal. Chem. 388 (2007) 1393–1414.
[24] K. Ridgway, S.P.D. Lalljie, R.M. Smith, J. Chromatogr. A 1153 (2007) 36–53.
[25] L.F. Cuevas-Glory, J.A. Pino, L.S. Santiago, E. Sauri-Duch, Food Chem. 103 (2007) 1032–1043.
[26] H. Kataoka, H.L. Lord, J. Pawliszyn, J. Chromatogr. A 880 (2000) 35–62.
[27] A.K. Malik, V. Kaur, N. Verma, Talanta 68 (2006) 842–849.
[28] H.B. Wan, H. Chi, M.K. Wong, C.Y. Mok, Anal. Chem. Acta 298 (1994) 219–223.
[29] Z. Tong, L. Guanghan, Y. Xin, Anal. Lett. 34 (2001) 627–634.
[30] R. Aranda, P. Kruus, R.C. Burk, J. Chromatogr. A 888 (2000) 35–41.
[31] D. Djozan, Y. Assadi, Chromatographia 60 (2004) 313–317.
[32] R.C. Sparrenberger, C.K. Cross, E.D. Conte, Anal. Chem. 76 (2004) 6156–6159.
[33] J. Wu, W.M. Mullett, J. Pawliszyn, Anal. Chem. 74 (2002) 4855–4859.
[34] G. Liljegren, L. Nyholm, Analyst 128 (2003) 232–236.
[35] M.A. Azenha, P.J. Nogueira, A.F. Silva, Anal. Chem. 78 (2006) 2071–2074.
[36] C. Dietz, J. Sanz, C. Camara, J. Chromatogr. A 1103 (2006) 183–192.
[37] G. Liljegren, N. Forsgard, C. Zettersten, J. Pettersson, M. Svedberg, M. Herranen, L. Nyholm, Analyst 130 (2005) 1358–1368.
[38] U. Tamer, N. Ertas, Y.A. Udum, Y. Sahin, K. Pekmez, A. Yildiz, Talanta 67 (2005) 245–251.
[39] F. Guo, T. GóRecki, D. Irish, J. Pawliszyn, Anal. Commun. 33 (1996) 361–364.
[40] 98/83/EC, Council Directive (98/83/EC) of 3 November 1998 relating to the quality of water intended for human consumption, Off. J. Eur. Commun. L330 (1998) 32–54.
[41] Z.-W. Yao, G.-B. Jiang, J.-M. Liu, W. Cheng, Talanta 55 (2001) 807–814.
[42] E. Ballesteros, M.J. Parrado, J. Chromatogr. A 1029 (2004) 267–273.
[43] C.P. Sanz, R. Halko, Z.S. Ferrera, J.J.S. Rodríguez, Anal. Chim. Acta 524 (2004) 265–270.
[44] Q. Xiao, B. Hu, C. Yu, L. Xia, Z. Jiang, Talanta 69 (2006) 848–855.
[45] M.R. Khalili-Zanjani, Y. Yamini, N. Yazdanfar, S. Shariati, Anal. Chim. Acta 606 (2008) 202–208.