Journal of Chromatography A, 1219 (2012) 61–65

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

Ultra-preconcentration and determination of thirteen organophosphorus pesticides in water samples using solid-phase extraction followed by dispersive liquid–liquid microextraction and gas chromatography with flame photometric detection

Soheila Samadi [a], Hassan Sereshti [a,*], Yaghoub Assadi [b]

[a] Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran
[b] Quality Control Department, Daana Pharmaceutical Company, P.O. Box 501575-5181, Tabriz, Iran

ARTICLE INFO

Article history:
Received 13 September 2011
Received in revised form
10 November 2011
Accepted 11 November 2011
Available online 19 November 2011

Keywords:
Dispersive liquid–liquid microextraction
Solid-phase extraction
Gas chromatography
Organophosphorus pesticides

ABSTRACT

An ultra-preconcentration technique composed of solid-phase extraction (SPE) and dispersive liquid–liquid microextraction (DLLME) coupled with gas chromatography–flame photometric detection (GC–FPD) was used for determination of thirteen organophosphorus pesticides (OPPs) including phorate, diazinon, disolfotane, methyl parathion, sumithion, chlorpyrifos, malathion, fenthion, profenphose, ethion, phosalone, azinphose-methyl and co-ral in aqueous samples. The analytes were collected from large volumes of aqueous solutions (100 mL) into 100 mg of a SPE C_{18} sorbent. The effective variables of SPE including type and volume of elution solvent, volume and flow rate of sample solution, and salt concentration were investigated and optimized. Acetone was selected as eluent in SPE and disperser solvent in DLLME and chlorobenzene was used as extraction solvent. Under the optimal conditions, the enrichment factors were between 15,160 and 21,000 and extraction recoveries were 75.8–105.0%. The linear range was 1–10,000 ng L^{-1} and limits of detection (LODs) were between 0.2 and 1.5 ng L^{-1}. The relative standard deviations (RSDs) for 50 ng L^{-1} of OPPs in water with and without an internal standard, were in the range of 1.4–7.9% (n = 5) and 4.0–11.6%, respectively. The relative recoveries of OPPs from well and farm water sat spiking levels of 25 and 250 ng L^{-1} were 88–109%.

1. Introduction

Organophosphorus (OP) compounds are cholinesterase inhibiting chemicals used as pesticides and also chemical warfare agents (nerve agents) [1]. High levels of pesticides are used every year in the production and post-production treatments of agricultural commodities [2]. OPPs usage is preferred over other pesticides despite their high toxicity because they exhibit moderate environmental persistence [3]. Determination of OPPs in water is usually performed by sample preparation methods coupled with gas chromatography–nitrogen phosphorus detection (GC–NPD) [4–8], gas chromatography–mass spectrometry (GC–MS) [9–14], GC–FPD [4,15–18] and high-performance liquid chromatography (HPLC) [19–23]. Before analysis, due to the complexity of some sample matrices, their in compatibility with the desired instrumental method and low concentrations of the analytes in water, a preliminary sample preconcentration and/or separation technique is required. Solid-phase extraction (SPE) [24,25], solid-phase microextraction (SPME) [26–28], cloud point extraction (CPE) [29–31], single drop microextraction (SDME) [32,33,17], ultrasound-assisted emulsification microextraction (USAEME) [34–37], vortex-assisted liquid–liquid microextraction (VALLME) [38–40], DLLME [18] and SPE in combination with DLLME [14] have been used for preparation of water samples containing OPPs. SPE–DLLME is an efficient hyphenated technique that offers the advantages of both methods such as simplicity, low solvent usage and exposure, low disposal costs and extraction time, with high recovery and enrichment factor.

In the present work, we also applied SPE–DLLME to parts per trillion (ppt) determinations of OPPs in aqueous solutions. The main special features of the present work over the similar study in Ref. [14] are: (i) 13 OPPs were investigated that only three of them (diazinon, methyl parathion and chlorpyrifos) are the same; (ii) the analysis method in the present work is GC–FPD (a selective detector towards OPPs), but in Ref. [14] GC–MS (a universal detector) was used; (iii) the effects of important SPE parameters such as type and volume of both solvents, sample flow rate, sample volume, and salt effect were studied and optimized, while extraction

* Corresponding author. Tel.: +98 21 61113632; fax: +98 21 66495291.
E-mail address: sereshti@khayam.ut.ac.ir (H. Sereshti).

0021-9673/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.11.019

solvent and elution/dispersion solvents nature and volume, water volume and sample volume were investigated in Ref. [14]; (iv) an internal standard (triphenylphosphate) was used to improve the measurement's precision. Finally, the performance of the present method for analysis of real samples was examined and the figures of merit were reported and compared with the previous reported studies.

2. Experimental

2.1. Reagents and standards

Organophosphorus pesticides such as phorate, diazinon, disolfotane, methyl parathion, sumithion, chlorpyrifos, malathion, fenthion, profenphose, ethion, phosalone, azinphose-methyl and co-ral were purchased from Polyscience (Niles, USA). Chlorobenzene, acetone, acetonitrile, methanol, sodium chloride, and triphenylphosphate (suprasolv for gas chromatography) were obtained from Merck chemicals (Darmstadt, Germany). These solvents were distillated at least three times before use. Double distilled water was used for preparation of aqueous solutions 0.01000 g of each analyte (OPPs) was dissolved in 10.0 mL methanol to prepare a standard solution of 1000 mg L^{-1}. A fresh standard solution of OPPs (1.00 mg L^{-1}) was prepared in methanol on the first day of every week and stored at 4 °C. Real water samples including farm and well waters were collected from Tehran (capital of Iran) and stored in dark at 4 °C, then analyzed within 48 h by the proposed method.

2.2. Instrumentation

GC analysis were carried out on a Shimadzu-2010 gas chromatograph (Tokyo, Japan) equipped with a split/splitless injector system, a flame photometric detector (FPD) and a ZB-35 capillary column with 30 m length, 0.25 mm internal diameter and 0.15 μm stationary film thickness (65% methyl–35% diphenylpolysiloxane copolymer) prepared from Phenomenex (Torrance, CA, USA) was used for separation and determination of OPPs. The oven temperature was held at 100 °C for 1 min then programmed at 25 °C min^{-1} to 150 °C, from 150 to 175 °C at the rate of 5 °C min^{-1}, from 175 to 195 °C at the rate of 2 °C min^{-1}, from 195 to 275 °C at the rate of 10 °C min^{-1} and finally held for 5 min. The total time for one GC run was 32 min. Other operating conditions were as follows: ultra pure helium (99.999%) supplied by Air Products (Crewe, UK), passed through a molecularsieve trap and oxygen trap from Chromatography Research Supplies (Kentucky, USA) was used as the carrier gas at constant linear velocity of 35 cm s^{-1}. The injection port temperature was 250 °C and used in splitless mode with splitless time of 0.5 min. The detector temperature was held at 300 °C. A hydrogen generator instrument model OPGU-2200s Shimadzu (Tokyo, Japan) was applied to supply hydrogen gas for FPD at a flow of 80 mL min^{-1}. The zero air as an oxidant for FPD was supplied by Air Products (Crewe, UK) with purity of 99.999% and flow rate of 120 mL min^{-1}. A centrifuge instrument, model 2010D Centurion Scientific (West Sussex, UK), was used for centrifugation. SPE of OPPs was performed by using 100 mg of C_{18} sorbent with a 3 mL syringe barrel was prepared from Varian (Harbor City, CA, USA). The glass test tubes that were used for extraction process maintained at 500 °C in a furnace model CWF 1200 Carbolite (Hope Valley, UK) to remove organic residues and well sediment of the dispersed extraction solvent in the centrifugation step.

2.3. The procedure

At first, a C_{18} SPE sorbent was conditioned with 2.0 mL of acetone and 2.0 mL of water, sequentially. Then, a 100 mL of the water sample containing 50 ng L^{-1} of OPPs and triphenylphosphate (internal standard) was loaded at a flow rate of 10 mL min^{-1} with the aid of a Rotavac vacuum pump (Heidolph, Germany). The C_{18} SPE cartridge was rinsed with 2 mL of double distilled water to remove the matrix interferences. After ventilating of the solid phase, the desired compounds were eluted with 1.00 mL acetone and were collected into a 10-mL screw cap glass test tube. A 12 μL of chlorobenzene was added to the test tube. The resulted mixture was drawn into a syringe and rapidly injected into a 5.00 mL of double distilled water in a 10 mL screw cap glass test tube with conic bottom. A cloudy solution, resulted from the dispersion of the tiny chlorobenzene droplets in the aqueous solution, was formed in the test tube. The mixture was then centrifuged for 2 min at 5000 rpm. By this process, the dispersed tiny chlorobenzene droplets were sedimented at the bottom of the conical test tube (5.0 ± 0.3 μL). Then, 0.50 μL of the sedimented phase were removed by a 1.00 μL microsyringe with zero dead volume and a cone tip needle prepared from SGE Analytical Science (Victoria, Australia) and injected into GC.

3. Results and discussion

In this work, SPE–DLLME–GC–FPD was applied to determination of OPPs as model compounds from water samples to investigate the performance of the proposed method. To achieve a high extraction recovery (ER) and enrichment factor (EF), the SPE–DLLME conditions were optimized. Since the DLLME main parameters were optimized in the previous research [18], the obtained results were used in this study. However, the SPE parameters such as type and volume of the elution solvent, flow rate of sample solution, sample volume and salt addition were investigated to find the optimal conditions. The relative recovery was used to evaluate the extraction efficiency under different conditions. The enrichment factor was calculated by using Eq. (1).

$$EF = \frac{C_{sed}}{C_0} \quad (1)$$

where EF, C_{sed} and C_0 are the enrichment factor, concentration of analyte in sedimented phase and initial concentration of analyte in aqueous sample, respectively. The C_{sed} was calculated by direct injection of OPPs standard solutions in chlorobenzene with concentrations in the range of 0.50–2.50 mg L^{-1}. The extraction recovery (ER) was defined as the percentage of the total analyte amount (n_0) which was extracted to the sedimented phase (n_{sed}).

$$ER = \frac{n_{sed}}{n_0} \times 100 = \left[\frac{(C_{sed} \times V_{sed})}{(C_0 \times V_{aq})}\right] \times 100 = EF \times \left(\frac{V_{sed}}{V_{aq}}\right) \times 100 \quad (2)$$

where V_{sed} and V_{aq} are the volume of sedimented phase and volume of aqueous sample, respectively. The relative recoveries were calculated using the following equation:

$$RR = \frac{C_{found} - C_{real}}{C_{added}} \times 100 \quad (3)$$

where C_{found}, C_{real}, and C_{added} are the concentrations of analyte after addition of known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of known amount of standard which was spiked to the real sample, respectively.

3.1. Effect of elution solvent type and volume

The elution solvent in the SPE step is used as the disperser solvent in DLLME. According to the previous studies and experiments, acetone, acetonitrile and methanol were examined for this purpose [18]. The solid phase was eluted by using 1.00 mL of the

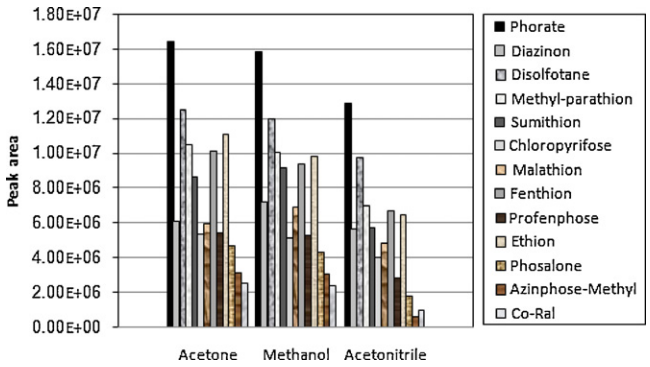

Fig. 1. Effect of the eluent solvent on the peak area of OPPs in SPE–DLLME.

elution solvents. Fig. 1 shows that the recovery (peak areas) of acetone is higher than acetonitrile and methanol. Additionally, it is less toxic and less expensive. Therefore, acetone was selected as elution solvent and disperser solvent. To determine the optimum volume of acetone to elute analytes from the SPE cartridge, the elution was carried out three times with 1.00 mL of acetone frequently. It was concluded that 1.00 mL of acetone was sufficient to desorb the trapped OPPs from the SPE cartridge.

3.2. Effect of breakthrough volume

The breakthrough volume (BTV) was studied by using different sample volumes (20, 50, 100, 150, 200 and 250 mL) of a standard solution of analytes (50 ng L^{-1}). The samples were preconcentrated on the Bond Elute C_{18} solid phase and then extracted by DLLME method. It was found that the recoveries of the OPPs were almost constant with different sample volumes. In order to have short and efficient experiments, a working volume of 100 mL was selected.

3.3. Effect of sample solution flow rate

The flow rate of sample solution through the solid phase is an effective parameter to control the analysis time. It must be low enough to perform an effective separation and high enough to shorten the time reasonably. The effect of flow rate on the extraction efficiency was studied in the range of 4–20 mL min^{-1}. The results showed that the OPPs recovery in this range was not affected considerably. To have an efficient analysis in a reasonable time, the sample flow rate of 10 mL min^{-1} was selected in the following experiments.

3.4. Salt addition

To investigate the effect of salt concentration on the recovery, the experiments were conducted at different salt (NaCl) contents of the sample solution, ranging from 0 to 10% (w/v). The results indicated that the salt addition had no significant effect on the extraction recoveries. Therefore, this method can be employed for separation and preconcentration of OPPs from saline solution up to 10% (w/v).

3.5. Analytical figures of merit

The calibration curves were prepared according to the procedure in Section 2.3 under the optimized conditions for a range of standard solutions from 1 to 20,000 ng L^{-1} at fourteen concentration levels. Two types of calibration curves were constructed: (i) without using internal standard, based on the peak area of analytes versus concentration; and (ii) with using an internal standard, based on the ratio of peak area of analytes to the peak area of the internal standard (triphenylphosphate) for each compound versus concentration (Table 1). Linear dynamic range (LDR) was between 1 and 10,000 ng L^{-1} for most of OPPs. The determination coefficients (R^2) were in the range of 0.9990–0.9999 with the internal standard and 0.9985–0.9998 without the internal standard. The repeatability was studied by extracting the spiked water sample (at concentration of 50 ng L^{-1}). The relative standard deviations (RSDs) were in the range of 1.4–7.9% and 4.0–11.6% with and without the internal standard ($n = 5$), respectively. The limit of detection (LODs) was defined as $C_{LOD} = 3S_d/m$, where C_{LOD}, S_d and m are LOD, standard deviation of the blank and slope of calibration graph, respectively. The LODs were obtained 0.2–1.5 ng L^{-1}. Moreover, the enrichment factors and the recovery were 15,160–21,000, and 75.8–105.0%, respectively.

3.6. Analysis of real samples

In order to investigate the matrix effect on the efficiency of method, well and farm waters were examined under the optimal

Table 1
Quantitative results of SPE–DLLME–GC–FPD for determination of OPPs from water sample.[a]

OPPs	RSD% [b] ($n = 5$)	RSD % [c] ($n = 5$)	EF [d]	R [e] (%)	LDR [f] (ng L^{-1})	r^2 [g]	r^2 [h]	LOD [i] (ng L^{-1})
Phorate	6.3	4.5	17,080	85.4	1–10,000	0.9993	0.9991	0.2
Diazinon	6.5	4.9	18,540	92.7	1–10,000	0.9995	0.9994	0.3
Disolfotane	2.6	5.5	18,100	90.5	1–10,000	0.9991	0.999	0.2
Methyl parathion	3.6	4.0	15,160	75.8	1–10,000	0.9995	0.9991	0.3
Sumithion	2.1	4.8	17,600	88	1–10,000	0.999	0.9985	0.3
Chlorpyrifose	7.2	7.1	17,780	88.9	1–10,000	0.9996	0.9992	0.3
Malathion	1.4	5.6	17,280	86.4	2–10,000	0.9998	0.9994	1.0
Fenthion	2.3	4.5	17,420	87.1	1–10,000	0.9997	0.9997	0.3
Profenphose	2.0	6.7	21,000	105	1–10,000	0.9995	0.9993	0.3
Ethion	4.3	4.4	16,580	82.9	1–10,000	0.9998	0.9995	0.2
Phosalone	7.9	11.6	19,120	95.6	1–10,000	0.9997	0.9994	0.3
Azinphose-methyl	2.2	5.1	16,100	80.5	5–10,000	0.9999	0.9998	1.5
Co-ral	6.8	10.6	19,460	97.3	5–10,000	0.9996	0.9995	1.5

[a] Extraction conditions: water sample volume 100 mL; eluent or disperser solvent (acetone) volume, 1.00 mL; extraction solvent (chlorobenzene) volume, 12.0 μL; sample solution flow rate, 10 mL min^{-1}; sedimented phase volume, 5.0 ± 0.3 μL; room temperature; concentration of internal standard (triphenylphosphate), 50.0 ng L^{-1}.
[b] With internal standard (concentration of OPPs, 50.0 ng L^{-1}).
[c] Without internal standard (concentration of OPPs, 50.0 ng L^{-1}).
[d] Enrichment factor.
[e] Recovery.
[f] Linear dynamic range.
[g] With internal standard.
[h] Without internal standard.
[i] Limit of detection.

Table 2
Relative recoveries and standard deviations of OPPs from spiked well and farm water samples.[a]

OPPs	Well water			Farm water		
	Added (ng L^{-1})	Found (SD[b], $n=3$) (ng L^{-1})	Relative recovery (%)	Added (ng L^{-1})	Found (SD[b], $n=3$) (ng L^{-1})	Relative recovery (%)
Phorate	25	24.1 (0.5)	96	250	257 (11)	103
Diazinon	25	25.2 (0.8)	101	250	265 (14)	106
Disolfotane	25	23.7 (0.7)	95	250	239 (10)	96
Methyl parathion	25	26.3 (0.2)	105	250	245 (7)	98
Sumithion	25	25.0 (1.5)	100	250	236 (18)	94
Chlorpyrifose	25	26.7 (1.1)	107	250	251 (14)	100
Malathion	25	27.2 (1.6)	109	250	272 (17)	109
Fenthion	25	25.4 (0.9)	102	250	247 (10)	99
Profenphose	25	24.9 (1.7)	100	250	258 (12)	103
Ethion	25	23.8 (1.4)	95	250	256 (15)	102
Phosalone	25	24.5 (1.8)	98	250	259 (21)	104
Azinphose-methyl	25	23.1 (2.1)	92	250	234 (20)	94
Co-ral	25	22.2 (2.5)	89	250	220 (24)	88

[a] Extraction conditions: water sample volume, 100 mL; eluent or disperser solvent (acetone) volume, 1.00 mL; sample solution flow rate, 10 mL min^{-1}; extraction solvent (chlorobenzene) volume, 12 μL; sedimented phase volume, 5.0 ± 0.3 μL; room temperature; concentration of internal standard (triphenylphosphate), 50.0 ng L^{-1}.
[b] Standard deviation.

Table 3
Comparison of SPE–DLLME–GC–FPD with other methods for determination of OPPs.

Methods	LOD[a] (ng L^{-1})	LDR[b] (μg L^{-1})	RSD[c] (%)	Ref.
SPME–GC–FPD	30–400	1.0–50	5.0–8	[26]
SDME–GC–MS	10.0–70	0.5–100	8.5–15	[32]
UASEME–HPLC–DAD	100–300	1–200	3.3–5.6	[36]
VSLLME–GC–FPD	10.0–50	0.1–50.0	2.3–8.9	[40]
DLLME–GC–FPD	3.0–20	0.01–100	4.6–6.5	[18]
SPE–DLLME–GC–MS	0.038–0.230	10–100	8.6–10.4	[14]
SPE–DLLME–GC–FPD	0.2–1.5	0.01–0.1	4.0–11.6	This work

[a] Limit of detection.
[b] Linear dynamic range.
[c] Relative standard deviation.

conditions. The samples were collected from Tehran (capital of Iran). The blank analysis showed that the samples were free of OPPs contamination. Therefore, they were spiked with the OPPs standard solutions at different concentration levels (25 and 250 ng L^{-1}). Fig. 2 shows the chromatograms obtained for well water and spiked well water at the concentration level of 25 ng L^{-1} for each of OPPs. The relative recovery of the OPPs from well and farm waters were in the range of 89–109% and 88–109%, respectively (Table 2). Therefore, the results indicated that the matrices of the analyzed real water samples had ignorable effect on the performance of the method.

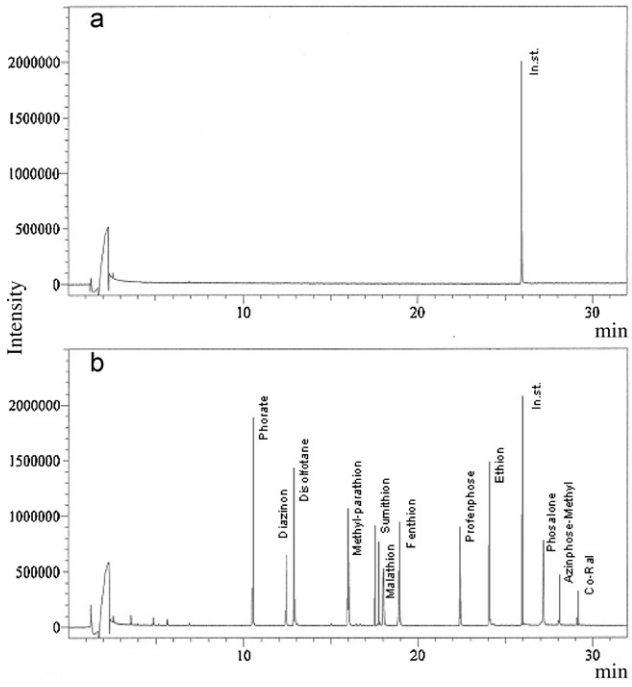

Fig. 2. Chromatogram of (a) well water and (b) spiked well water, with 25.0 ng L^{-1} of each OPPs, obtained by SPE–DLLME–GC–FPD method. Extraction conditions: extraction solvent (chlorobenzene) volume, 12 μL; eluent (acetone) volume, 1.00 mL; sediment phase volume, 5.0 ± 0.3 μL; water sample volume, 100 mL; sample solution flow rate, 10 mL min^{-1}.

3.7. Comparison of SPE–DLLME with other methods

A comparison of the main analytical characteristics of the proposed method with other previously studied techniques for determination of OPPs in water samples is summarized in Table 3. The LOD and LDR in this work are considerably lower than that of the most of the other methods. RSD is better than some and comparable with those of the other studies. It can be concluded that SPE–DLLME–GC–FPD is a sensitive method that can be used for the ultra precocentration and determination of OPPs from water samples.

4. Conclusions

In the present work, SPE–DLLME technique coupled with GC–FPD was used for separation, preconcentration and determination of simultaneous thirteen OPPs in water samples. A comparison with other previously reported studies indicated that the proposed method is fast and simple, specified with a very high enrichment factor (about 20,000), ultra preconcentration factor, low LOD, relatively wide LDR and short analysis time. The excellent performance of the method in the analysis of the real samples showed that it can be applied in complex matrices (such as highly saline solutions) successfully. Considering its advantages, this new developed method is a high performance preconcentration technique

for determination of ultra trace organic compounds in real water samples.

References

[1] R. Rahimi, M. Abdollahi, Pestic. Biochem. Physiol. 88 (2007) 115.
[2] M. Silvia Dĭıaz-Cruz, Dami'a Barcelĭo, J. Chromatogr. A 1132 (2006) 21.
[3] R.D. Wauchope, T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, J.P. Burt, Rev. Environ. Contam. Toxicol. 123 (1992) 1.
[4] D. Barcelo, J. Chromatogr. 643 (1993) 17.
[5] I. Valor, J.C. Moltoĭ, D. Apraiz, G. Font, J. Chromatogr. A 767 (1997) 195.
[6] H. Tsoukali, G. Theodoridis, N. Raikos, I. Grigoratou, J. Chromatogr. B 822 (2005) 194.
[7] U. Uygun, B. Senoz, H. Koksel, Food Chem. 109 (2008) 355.
[8] U. Uygun, B. Senoz, S. Öztürk, H. Koksel, Food Chem. 117 (2009) 261.
[9] H.G.J. Mol, R.C.J. van Dam, O.M. Steijger, J. Chromatogr. A 1015 (2003) 119.
[10] F. Hernández, J.V. Sancho, O.J. Pozo, J. Chromatogr. B 808 (2004) 229.
[11] M.P. García de Llasera, M.L. Reyes-Reyes, Food Chem. 114 (2009) 1510.
[12] R. Su, X. Xu, X. Wang, D. Li, X. Li, H. Zhang, A. Yu, J. Chromatogr. B 879 (2011) 3423.
[13] F.M. Rodrigues, P.R.R. Mesquita, L.S. de Oliveira, F.S. de Oliveira, A.M. Filho, P.A.P. Pereira, J.B. de Andrade, Microchem. J. 98 (2011) 56.
[14] A.C.H. Alves, M.M.P.B. Gonçalve, M.M.S. Bernardo, B.S. Mendes, J. Sep. Sci. 34 (2011) 2475.
[15] K. Patel, R.J. Fussell, R. Macarthur, D.M. Goodall, B.J. Keely, J. Chromatogr. A 1046 (2004) 225.
[16] G. Dugo, G. Di Bella, L. La Torre, M. Saitta, Food Control 16 (2005) 435.
[17] F. Ahmadi, Y. Assadi, S.M.R. Milani Hosseini, M. Rezaee, J. Chromatogr. A 1101 (2006) 307.
[18] S. Berijani, Y. Assadi, M. Anbia, M.R. Milani Hosseini, E. Aghaee, J. Chromatogr. A 1123 (2006) 1.
[19] C. Aquilar, I. Ferrer, F. Borrull, R.M. Marce, D. Barcelo, Anal. Chim. Acta 386 (1999) 237.
[20] T. Pérez-Ruiz, C. Martínez-Lozano, V. Tomás, J. Martín, Anal. Chim. Acta 540 (2005) 383.
[21] L. He, X. Luo, H. Xie, C. Wang, X. Jiang, K. Lu, Anal. Chim. Acta 655 (2009) 52.
[22] M. Tankiewicz, J. Fenik, M. Biziuk, Trends Anal. Chem. 29 (2010) 1050.
[23] T.M. Gutiérrez Valencia, M.P.G. de Llasera, J. Chromatogr. A 1218 (2011) 6869.
[24] E. Ballesteros, M.J. Parrado, J. Chromatogr. A 1029 (2004) 267.
[25] P. Georgakopoulos, R. Zachari, M. Mataragas, P. Athanasopoulos, E.H. Drosinos, P.N. Skandamis, Food Chem. 128 (2011) 536.
[26] P.G. Su, S.D. Huang, Talanta 49 (1999) 393.
[27] F. Zhu, W. Ruan, M. He, F. Zeng, T. Luan, Y. Tong, T. Lu, G. Ouyang, Anal. Chim. Acta 650 (2009) 202.
[28] F.M. Rodrigues, P.R.R. Mesquita, L.S. de Oliveira, F.S. de Oliveira, A.M. Filho, P.A. de, P. Pereira, J.B. de Andrade, Microchem. J. 98 (2011) 56.
[29] R. Carabias-Martinez, E. Rodriguez-Gonzalo, B. Moreno-Cordero, J.L. Perez-Pavon, C.C. Garcia-Pinto, E. Fernandez-Laespada, J. Chromatogr. A 902 (2000) 251.
[30] C. Padrón Sanz, R. Halko, Z. Sosa Ferrera, J.J. Santana, Rodrıĭguez, Anal. Chim. Acta 524 (2004) 265.
[31] W. Zhao, X. Sun, X. Deng, L. Huang, M. Yang, Z. Zhou, Food Chem. 127 (2011) 683.
[32] D.A. Lambropoulon, E. Psillakis, T.A. Albanis, N. Kalogerakis, Anal. Chim. Acta 516 (2004) 205.
[33] Q. Xiao, B. Hu, C. Yu, L. Xia, Z. Jiang, Talanta 69 (2006) 848.
[34] J. Regueiro, M. Llompart, C. Garcia-Jares, J.C. Garcia-Monteagudo, R. Cela, J. Chromatogr. A 1190 (2008) 27.
[35] A.I. García-Valcárcel, J.L. Tadeo, Anal. Chim. Acta 641 (2009) 117.
[36] C. Wu, N. Liu, Q. Wu, C. Wang, Z. Wang, Anal. Chim. Acta 679 (2010) 56.
[37] C. Jia, X. Zhv, L. Chen, M. He, P. Yu, E. Zhao, J. Sep. Sci 33 (2010) 244.
[38] E. Yiantzi, E. Psillakis, K. Tyrovola, N. Kalogerakis, Talanta 80 (2010) 2057.
[39] C. Jia, X. Zhua, J. Wang, E. Zhao, M. He, L. Chena, P. Yu, J. Chromatogr. A 1217 (2010) 5868.
[40] Z.-H. Yang, Y.-L. Lu, Y. Liu, T. Wu, Z.-Q. Zhou, D.-H. Liu, J. Chromatogr. A, in press.