Chromatographia (2011) 73:385–391
DOI 10.1007/s10337-010-1885-2

FULL SHORT COMMUNICATION

Development of an Analytical Method Based on Accelerated Solvent Extraction, Solid-Phase Extraction Clean-Up, then GC–ECD for Analysis of Fourteen Organochlorine Pesticides in Cereal Crops

Yaping Zhang · Jun Yang · Ronghua Shi · Qingde Su · Yun Gao · Xiaolan Zhu

Received: 16 September 2010 / Revised: 24 October 2010 / Accepted: 10 December 2010 / Published online: 9 January 2011

Abstract A method has been developed for analysis of 14 organochlorine pesticide residues in cereals. After accelerated solvent extraction and solid-phase extraction clean-up on graphitized carbon black/primary–secondary amine (GCB/PSA), to reduce co-extraction of interferences, pesticide residues were analyzed by gas chromatography with electron-capture detection. When the method was validated, recoveries were in the range 78–116%, relative standard deviations were in the range 1.1–16.3%, and limits of detection and quantification were from 1.5 to 4.2 μg kg^{-1} and from 4.6 to 12.5 μg kg^{-1}, respectively.

Keywords Gas chromatography–electron-capture detection · Accelerated solvent extraction · Solid-phase extraction · Cereals · Organochlorine pesticide residues

Introduction

Cereals constitute more than 60% of total worldwide agricultural production, and are the most important annual seed crop. Rice and wheat are the most important staple food crops of the world. These and maize are the three most important cereals, and more than 500 million tons of each is produced annually worldwide, mainly in Asia. Several countries largely depend on importing cereal crops [1].

Organochlorine pesticides (OCPs) have been applied worldwide and in quantity to crops to avoid losses, and have ensured production since the 1940s [2, 3]. These pesticides tend to bioaccumulate in the food chain, however, and are stored in fat because of their persistent and lipophilic characteristics [4–6]. Even the lowest levels of pesticide residues in food may be highly dangerous to humans. Use of these compounds has been forbidden, because of their low biodegradability, high persistence, and toxicity, which includes cancer-inducing and endocrine-disrupting properties. Maximum recommended limits (MRLs) for OCP residues in a variety of agricultural products have been established by the European Union; in the most severe cases these concentrations can be as low as 10 μg kg^{-1} [7–9]. There are still reports of detection of OCPs in water [10], soil [11, 12] and food [7, 13, 14], however, and the residues continue to have a significant effect on food safety and international trade [2].

Chawla et al. [15] proposed a method using Soxhlet extraction (SE), silica gel clean-up and GC–ECD for analysis of DDT and HCH in wheat flour. Mastovska et al. [16] developed a method that used extraction by shaking in a separating funnel and dispersive solid-phase extraction combined with GC–TOF–MS and UPLC–MS–MS for analysis of pesticide multiresidues in cereal grain. A method for analysis of six OCPs in cereals using dynamic microwave-assisted extraction coupled with on-line solid-phase extraction then high-performance liquid chromatography has been reported [17]. Usually, however, these methods are costly, because of the large amounts of solvents and other expensive consumables used, hazardous, and the level of automation is low, because of the conventional extraction procedures used. It is, therefore, necessary to establish faster methods with easy work-up for cost-effective, less harmful, and sensitive simultaneous analysis of OCP residues in cereals.

Although many methods for analysis of pesticides in fruit, vegetables, and other matrices have been described,

Y. Zhang · J. Yang (✉) · R. Shi · Q. Su · Y. Gao · X. Zhu
Department of Chemistry, University of Science and Technology of China, Hefei 230026, People's Republic of China
e-mail: yjun8202@ustc.edu.cn

analysis of pesticide residues is still an analytical challenge. In recent years, many new techniques, for example accelerated solvent extraction (ASE) [18], microwave-assisted extraction (MAE) [17, 18], and supercritical-fluid extraction (SFE) [19] have been used for analysis of OCPs in many sample matrices. Compared with traditional methods these extraction techniques have advantages such as reduction of the volume of extraction solvents and time of analysis, a high level of automation, and improvement of the reproducibility of compound recovery [19]. ASE, developed by Richter in 1995, is performed at temperatures above the solvent boiling point and at pressures above atmospheric pressure. This improves penetration of the matrix by the solvent, and thus dissolution of compounds present in the sample, leading to results better than or comparable with those obtained by use of Soxhlet extraction and other techniques [20]. In recent years, ASE has been widely used to extract OCPs from different matrices—fruit [21], vegetables [18], soil [11, 12], food [22], animal feed [23], etc., and it is used in US Environmental Protection Agency (EPA) method 3,545 for analysis of organic compounds in solid matrices [20].

Because of the great extracting power of ASE, the extract obtained contains numerous interfering substances, which makes its purification mandatory. The methods of purification most commonly used are solvent–solvent extraction (SSE), gel-permeation chromatography (GPC) [24], and solid-phase extraction (SPE) with glass columns or commercial cartridges. SSE consumes large amounts of solvents, disposal of which is environmentally hazardous. GPC is costly and is always combined with other clean-up procedures [25]. Compared with such clean-up techniques, SPE has advantages of, for example, simplicity, speed, efficient use of solvents, and use of different types of adsorbent to meet the needs of the analysis.

The objective of this study was to establish and validate a method based on ASE with SPE purification for analysis of OCPs in cereals, to meet the European MRLs. Three different extraction methods, ASE, high-speed homogenizer extraction (HSHE), and SE were compared to determine their efficiency of extraction of OCPs from cereals. Four different SPE systems (GCB/PSA, carbon-GCB, alumina-N, and Florisil; all CNWBOND cartridges) were compared to achieve selective, simple, automated, low cost, and rapid separation of OCPs from the bulk of the matrixes. There have been no reports of use of GCB/PSA and GCB for clean-up of cereals. Finally, ASE–GCB/PSA was used for extraction and clean-up, and GC–ECD was used for quantitative analysis of the OCPs in the purified extracts, owing to the sensitivity and selectivity of ECD. Nine samples from different parts of China were analyzed by use of the method.

Experimental

Reagents and Materials

A standard mixture of eight OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, *p*,*p*′-DDD, *p*,*p*′-DDE, *o*,*p*′-DDT, and *p*,*p*′-DDT) and individual standards of α-endosulfan, β-endosulfan, heptachlor, heptachlor epoxide, dieldrin, and aldrin were purchased from the Agro-Environment Protection and Monitor Ministry (Tianjing, China). 2,4,5,6-Tetrachloro-*m*-xylene (TCMX; purity >98.5%), used as internal standard (IS), was supplied by Dr Ehrenstorfer (Augsburg, Germany).

Stock solutions containing β-HCH, *o*,*p*′-DDT, *p*,*p*′-DDD, heptachlor, heptachlor epoxide α-endosulfan, β-endosulfan, dieldrin, and aldrin at 1.5 μg mL^{-1}, α-HCH at 0.6 μg mL^{-1}, γ-HCH and δ-HCH at 0.9 μg mL^{-1}, *p*,*p*′-DDE at 1.2 μg mL^{-1}, and *p*,*p*′-DDT at 2.25 μg mL^{-1} were prepared in *n*-hexane. These stock solutions were diluted 5, 10, 50, 100, and 400 times with *n*-hexane to prepare standard solutions for calibration. All stock solutions and working standard solutions were stored at −18 and +4 °C, respectively.

The SPE cartridges investigated for the clean-up step were GCB/PSA, 6 mL (500 mg/500 mg), carbon-GCB, 12 mL (1 g), alumina-N, 3 mL (1 g), and Florisil, 6 mL (1 g) (all CNWBOND cartridges from CNW Technologies, Düsseldorf, Germany).

Cereal samples were collected from different areas of China, ground to a powder, sieved through a 40-mesh sieve, then stored at room temperature in glass vessels in the dark until analysis.

n-Hexane and acetonitrile (HPLC-grade) were obtained from Tedia (Fairfield, USA). Acetone, ethyl acetate, sodium sulfate (Na_2SO_4), and sodium chloride (NaCl) were analytical grade from China National Medicine (Beijing, China). Na_2SO_4 was heated at 650 °C for 4 h and NaCl at 600 °C for 6 h. These were then stored in a desiccator before use. Deionized water was used throughout.

Gas Chromatography

GC–ECD was performed with a Finnigan (Kansas, USA) Trace GC Ultra chromatograph equipped with a ^{63}Ni electron-capture detector, an autosampler, a split–splitless injector, operated in splitless mode, and programmed pneumatic control, all under computer control. Compounds were separated on a 30 m × 0.25 mm i.d. capillary column coated with a 0.25-μm film of DB-5 (J&W, Folsom, CA, USA).

Helium (99.999%) was used as carrier gas at a flow rate of 1.4 mL min^{-1}. The oven temperature was held at 100 °C for 1 min then programmed at 5 °C min^{-1} to 190 °C, which was held for 15 min, and then at 3 °C min^{-1}

Table 1 Concentrations (μg kg^{-1}) of OCP residues measured in real samples after extraction by ASE, HSHE, and SE ($n = 3$)

Pesticide	Sample 1 ($n = 3$)			Sample 2 ($n = 3$)		
	ASE (RSD, %)	HSHE (RSD, %)	SE (RSD, %)	ASE (RSD, %)	HSHE (RSD, %)	SE (RSD, %)
α-Endosulfan	24.1 (7.5)	12.7 (4.7)	18.5 (11.8)	ND	ND	ND
Dieldrin	ND	ND	ND	9.9 (2.2)	6.1 (9.3)	10.2 (5.7)
p,p′-DDE	6.3 (10.4)	3.1 (11.2)	7.8 (12.1)	21.1 (5.8)	11.0 (11.9)	10.4 (8.8)
p,p′-DDT and *o,p′*-DDT	12.5 (5.1)	9.0 (15.2)	13.1 (8.7)	ND	ND	ND

ND Not detected

to 270 °C. The injector temperature was 270 °C and the ECD temperature was 340 °C. The make up gas was nitrogen (99.999%) at a flow rate of 60 mL min^{-1}. The volume injected was 1 μL.

Sample Preparation

Automated ASE was performed with an ASE 300 system with 34-mL stainless steel extraction (Dionex, Sunnyvale, USA). Samples (1.00 g) were mixed in a mortar with 2.00 g sodium sulfate and the mixture was added directly to the extraction cell containing cellulose extraction filters to prevent frit blockage by breakthrough of fine powder into the collection bottle. Extraction was performed under the optimized conditions: extraction solvent *n*-hexane–acetone 1:1 (*v*/*v*), temperature 110 °C, pressure 10.34 MPa (1,500 psi), static time 5 min, heat-up time 5 min, flush volume 60%, purge N_2 for 60 s, and number of cycles 2. Finally the extracts were filtered and concentrated to 1.00 mL in *n*-hexane by rotary evaporation for the clean-up step.

High-speed homogenizer extraction was performed with a FSH-Ⅱ high-speed homogenizer from Huanyu Factory (Jiangsu, China). The sample (1.00 g) was placed in the blender in a mixture of 2.00 mL distilled water and 8.00 mL acetonitrile and homogenized for 2 min at 20,000 rpm. After extraction, 2.00 g sodium chloride was added and the mixture was shaken vigorously for 2 min then centrifuged for 5 min at 3500 rpm. The acetonitrile was evaporated to a droplet by rotary evaporation and then to dryness by means of a nitrogen stream, Finally, the residue was dissolved in 1.00 mL *n*-hexane for the clean-up step.

For Soxhlet extraction (SE), 1.00 g sample was placed in a glass fiber thimble and extracted with 200 mL hexane–acetone 1:1 (*v*/*v*) for 24 h. After cooling, the extract was concentrated to 1.00 mL in *n*-hexane by rotary evaporation for the clean-up step.

For clean-up, the concentrated extracts obtained as described above were applied to CNWBOND GCB/PSA SPE cartridges and the pesticides were eluted with 15 mL *n*-hexane–ethyl acetate 7:3 (*v*/*v*). The eluates were evaporated to a droplet by rotary evaporation and then to dryness by means of a gentle nitrogen stream. The residues were dissolved in 1 mL *n*-hexane, and the solution was filtered through a 0.45-μm pore-size PTFE syringe filter before GC–ECD analysis.

Results and Discussion

Comparison of ASE, HSHE, and SE

Extraction can vary in selectivity, efficiency, speed, and convenience and depends not only on the technique and conditions used but on the geometric configuration of the extraction phase [26]. In this work, ASE, HSHE, and SE were used to extract OCPs from the same real samples before quantification by GC–ECD. Table 1 shows the quantitative results, in μg kg^{-1} obtained by use of the three extraction methods for wheat flour. GC–ECD chromatograms obtained from unspiked samples after use of ASE, HSHE, and SE are shown in Fig. 1.

As shown in Table 1, the amounts of OCPs extracted by ASE and SE are mostly similar, but these are very different from those obtained by use of HSHE, especially for α-endosulfan, *p,p′*-DDT, and dieldrin, amounts of which were much lower than were obtained by ASE and SE. The chromatograms obtained after use of the three extraction techniques were comparable, as is clearly apparent from Fig. 1. With ASE more extraneous compounds were co-extracted from the matrix than by SE and HSHE, but these did not interfere with analysis of the pesticides, as is shown in Fig. 1d, from which it can be seen the analytes are separated sufficiently except for *o,p′*-DDT and *p,p′*-DDT. More extraneous compounds may be extracted because the elevated temperature and pressure during ASE extraction promote penetration of the sample by the solvent, forcing it into regions that would not normally be contacted under atmospheric conditions [1], improving the extraction efficiency by increasing dissolution of the compounds. Although cleaner extracts were obtained by SE, the extraction technique consumed large amounts of solvents, which could lead to environmental contamination, took a long time, and automation was difficult.

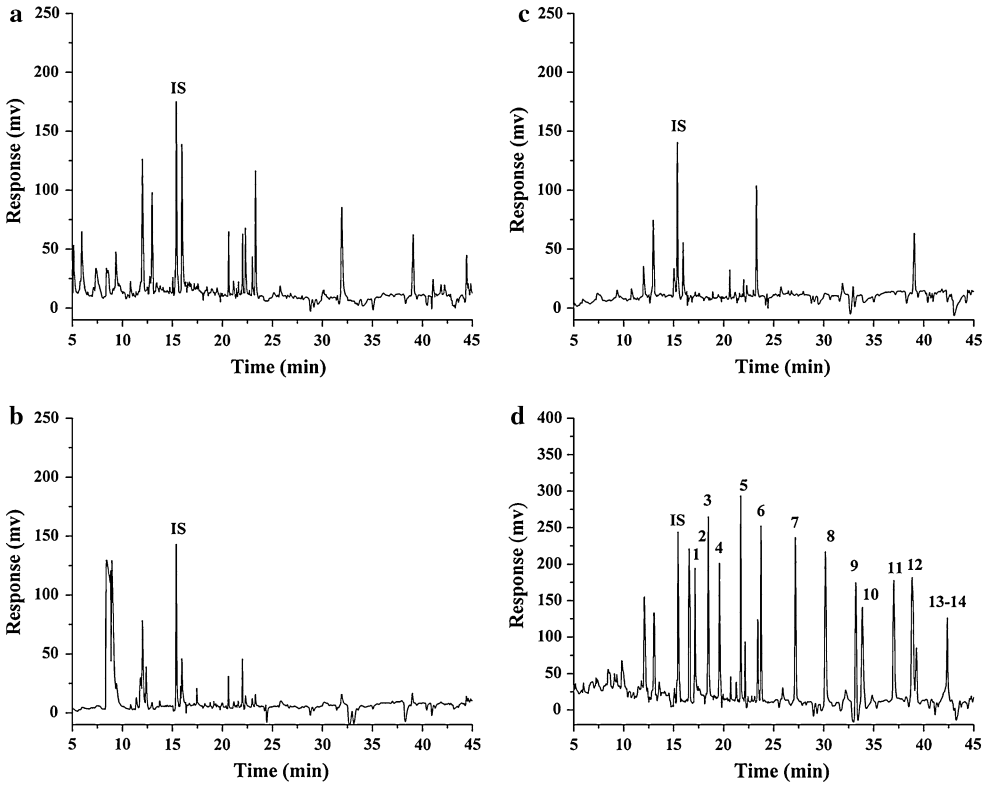

Fig. 1 GC–ECD chromatograms obtained from a wheat sample after use of the three different methods of extraction: **a** ASE; **b** HSHE; **c** SE; **d** ASE of spiked sample extract. *IS* 2,4,5,6-Tetrachloro-*m*-xylene, *1* α-HCH, *2* β-HCH, *3* γ-HCH, *4* δ-HCH, *5* heptachlor, *6* aldrin, *7* heptachlor epoxide, *8* α-endosulfan, *9* dieldrin, *10* *p*,*p*′-DDE, *11* β-endosulfan, *12* *p*,*p*′-DDD, *13*, *14* *o*,*p*′-DDT/*p*,*p*′-DDT

Optimization of Clean-Up

Owing to the complex cereal matrix and high extraction efficiency of ASE, it is very important to reduce the number of interferences before chromatographic analysis, because these can damage the chromatographic column and result in matrix effects [20]. Clean-up experiments were conducted to find the best adsorbent for SPE. For this purpose the adsorbents considered were commercial CNWBOND cartridges—GCB/PSA (500 mg/500 mg), carbon-GCB (1 g), alumina-N, and Florisil (1 g). Hexane–ethyl acetate 7:3 (*v*/*v*) was used as the elution solvent on the basis of optimization and other work [18, 20]. Recoveries of all 14 OCPs from the GCB/PSA, Florisil, carbon-GCB SPE, and alumina-N SPE cartridges were in the range 91.0–119.7, 78.4–114.8, 11.7–197.3, and 35.2–121.9%, respectively, with average RSD up to 3.7, 10.8, 20.2, and 8.9%, respectively. There was no significant difference between the results obtained from the GCB/PSA and Florisil cartridges, and recovery from these was better than from carbon-GCB and alumina-N. Very low clean-up recovery of aldrin (11.7%), very high clean-up recovery for γ-HCH (197.3%), and poor average RSD values were obtained when the carbon-GCB cartridge was used. These low values could be attributed to matrix interference; this resulted in an unstable baseline which hid the peaks. The high values may be attributed to several causes. The first might be the poor separation of these pesticides from interferences, which would result in overestimation. Another reason could be a matrix effect on transfer of compounds from the injection port, because major components may compete for the active sites of the liner, enabling transfer of larger amounts of analytes into the column. Interferences may also be the cause of the poor RSD, in agreement with another report [27]. Clean-up with the alumina-N cartridge resulted in the lowest recovery of aldrin (35.2%), and *o*,*p*′-DDT and *p*,*p*′-DDT (44.0% in total), much lower than for GCB/PSA and Florisil. The reason was that some of the most polar pesticides were not quantitatively eluted from the alumina columns [28].

GC–ECD chromatograms obtained from unspiked matrix after use of all the adsorbents are shown in Fig. 2, from which it is apparent there were important differences among the chromatograms. When GCB/PSA was used the chromatogram was cleaner than for the other adsorbents. The chromatogram obtained after use of the carbon-GCB cartridge contained peaks which interfered with the target compound peaks. The efficiency of clean-up step was in the order:

$$\text{GCB/PSA} > \text{Florisil} \approx \text{alumina-N} \geq \text{carbon-GCB}$$

This may be because the GCB/PSA cartridge is a dual-layer cartridge containing both GCB (upper layer) and PSA (lower layer) separated by a polyethylene frit. The GCB layer can remove most of the visible plant pigments but does little to eliminate fatty acids; the PSA layer, however, significantly retains fatty acids, organic acids, sugars, and some polar pigments [27, 29], hence the combination of GCB and PSA was found to provide the best clean-up of

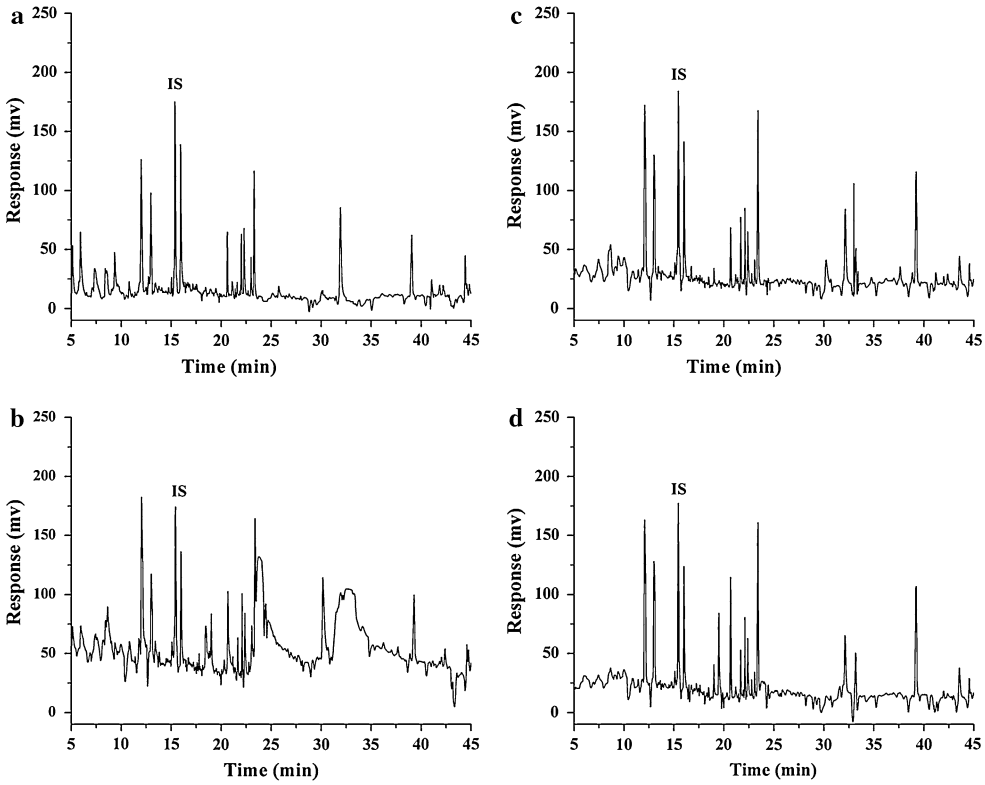

Fig. 2 GC–ECD chromatograms obtained from a wheat sample after SPE purification: **a** GCB/PSA, **b** carbon-GCB, **c** Florisil, **d** alumina-N. *IS* 2,4,5,6-tetrachloro-*m*-xylene

the matrix compounds in this study, and it was selected for the purification procedure.

Method Performance

Limits of Detection (LOD) and Quantification (LOQ), and Linearity

The linear ranges of the calibration plots for most of the OCPs were from 0.00375 to 0.300 μg mL^{-1}; for some of OCPs the ranges were from 0.00275 to 0.180 μg mL^{-1}, wider than in other work [3, 7, 18]. The linearity of the calibration plots over these concentration ranges were apparent from correlation coefficients (R^2) ranging between 0.9914 and 0.9990.

LOD and LOQ, are shown in Table 2, were calculated as the amounts for which the signals were 3 and 10 times the standard deviation above the blank signal from a GC–ECD injection. The values obtained were lower than 4.2 and 12.5 μg kg^{-1}, respectively, which were adequate for analysis of cereals containing the target compounds at the MRLs stipulated by the EU standard and the Japanese "Positive List System".

Repeatability

Recovery efficiency is important when an analytical method is evaluated. To assess the repeatability of this ASE–SPE–GC–ECD method, experiments were performed using spiked cereal sample. Analytical recovery (%) and RSD (%) obtained for the OCPs are listed in Table 2. In most cases, recovery of the pesticides was between 80 and 115%. Recovery from samples spiked at low and high spiked levels were 78.9–111.9 and 83.9–115.8%, respectively. RSDs for these two levels were in the ranges 1.8–16.4 and 1.1–10.3%.

Analysis of Real Samples

To assess the applicability of the method to real samples, nine samples of rice, wheat, and maize from different areas of China, were analyzed. α-Endosulfan, dieldrin, *p*,*p*′-DDE, *o*,*p*′-DDT, and *p*,*p*′-DDT were detected, all at concentrations lower than MRLs established by EU except for dieldrin. Although use of dieldrin was banned several years ago, unacceptable values may be because dieldrin was in widespread use in China from the 1960s to the 1980s and it is a very persistent organic pollutant.

Conclusions

A procedure based on ASE and SPE has been developed for analysis of OCPs in cereals. The high extraction efficiency of ASE combined with good purification on CNWBOND GCB/PSA resulted in satisfactory recovery,

Table 2 Recoveries and RSDs of 14 OCPs after use of the ASE–SPE–GC–ECD method

Pesticide	Spiked (mg kg^{-1})	Recovery (%)	RSD (%, $n = 3$)	Spiked (mg kg^{-1})	Recovery (%)	RSD (%, $n = 3$)	LOD (μg kg^{-1})	LOQ (μg kg^{-1})
α-HCH	0.012	107.0	4.1	0.030	85.1	3.5	1.5	4.6
β-HCH	0.030	86.8	3.0	0.075	83.9	2.8	1.9	5.6
γ-HCH	0.018	78.9	7.7	0.045	84.1	1.1	1.8	5.4
δ-HCH	0.018	108.6	8.8	0.045	88.7	4.5	1.8	5.4
Heptachlor	0.030	87.9	15.3	0.075	98.8	1.6	3.4	10.3
Aldrin	0.030	95.3	7.9	0.075	114.5	1.8	4.2	12.5
Heptachlor epoxide	0.030	91.7	4.8	0.075	112.0	3.6	1. 7	5.1
α-Endosulfan	0.030	88.0	4.9	0.075	92.0	2.2	2.0	5.9
Dieldrin	0.030	111.9	8.1	0.075	115.8	1.9	1.6	5.0
p,*p*′-DDE	0.024	93.3	7.5	0.060	103.9	3.1	1.9	5.7
β-Endosulfan	0.030	110.3	5.1	0.075	111.0	2.3	2.8	8.4
p,*p*′-DDD	0.030	101.3	1.8	0.075	98.3	5.5	3.9	11.8
p,*p*′-DDT and *o*,*p*′-DDT	0.045	82.4	16.4	0.11	103.8	10.3	2.4	7.2

clean chromatograms, and good selectivity and accuracy. Recovery was from 78 to 116% for samples spiked at levels between 0.0120 and 0.1125 mg kg^{-1}. RSD were below 16.4%, and LOD and LOQ were below 4.2 and 12.5 μg kg^{-1}, respectively. Moreover, compared with use of HSHE and SE for extraction, this method had advantages of lower cost, shorter analysis time, lower solvent consumption, and greater automation. It was demonstrated that the method met the requirements of multi-pesticide analysis.

Acknowledgments The authors gratefully acknowledge financial support from the Ministry of Science and Technology of Anhui province, P.R. China (project no. 08020303056).

References

1. Cho SK, El-Aty AMA, Park YS, Choi JH, Khay S, Kang CA, Park BJ, Kim SJ, Shim JH (2007) Biomed Chromatogr 21:602–609. doi:10.1002/bmc.792
2. Bakore N, John PJ, Bhatnagar P (2004) Environ Monit Assess 98:381–389. doi:10.1023/B:EMAS.0000038197.76047.83
3. Barriada-Pereira M, González-Castro MJ, Muniategui-Lorenzo S, López-Mahía P, Prada-Rodríguez D, Fernández-Fernández E (2004) J Chromatogr A 1061:133–139. doi:10.1016/j.chroma.2004.10.081
4. Zietz BP, Hoopmann M, Funcke M, Huppmann R, Suchenwirth R, Gierden E (2008) Int J Hyg Environ Health 11:624–638. doi:10.1016/j.ijheh.2008.04.001
5. Nakata H, Hirakawa Y, Kawazoe M, Nakabo T, Arizono K, Abe SI, Kitano T, Shimada H, Watanabe I, Li W, Ding X (2005) Environ Pollut 133:415–429. doi:10.1016/j.envpol.2004.07.003
6. Pérez-Serradilla JA, Mata-Granados JM, de Castro MDL (2010) Chromatographia 71:899–905. doi:10.1365/s10337-010-1575-0
7. Wang GQ, Zhang DF, Wang SF, Sun YA, Sun XL (2009) Chromatographia 69:1347–1351. doi:10.1365/s10337-009-1059-2
8. Húšková R, Matisová E, Kirchner M (2008) Chromatographia 68:S49–S55. doi:10.1365/s10337-008-0562-1
9. Vidal JLM, Espada MCP, Frenich AG, Arrebola FJ (2000) J Chromatogr A 867:235–245. doi:10.1016/S0021-9673(99)01082-1
10. Toledano RM, Cortés JM, Andini JC, Villén J, Vázquez A (2010) J Chromatogr A 1217:4738–4742. doi:10.1016/j.chroma.2010.05.011
11. Rashid A, Nawaz S, Barker H, Ahmad I, Ashraf M (2010) J Chromatogr A 1217:2933–2939. doi:10.1016/j.chroma.2010.02.060
12. Hussen A, Westbom R, Megersa N, Mathiasson L, Björklund E (2007) J Chromatogr A 1152:247–253. doi:10.1016/j.chroma.2007.02.076
13. García-Rodríguez D, Carro-Díaz AM, Lorenzo-Ferreira RA, Cela-Torrijos R (2010) J Chromatogr A 1217:2940–2949. doi:10.1016/j.chroma.2010.02.061
14. Kim MS, Kang TW, Pyo H, Yoon J, Choi K, Hong J (2008) J Chromatogr A 1208:25–33. doi:10.1016/j.chroma.2008.08.067
15. Chawla RP, Joia BS, Kalra RL (1979) Bull Environ Contam Toxicol 22:833–837. doi:10.1007/BF02027033
16. Mastovska K, Dorweiler KJ, Lehotay SJ, Wegscheid JS, Szpylka KA (2010) J Agric Food Chem 58:5959–5972. doi:10.1021/jf9029892
17. Chen LG, Ding L, Jin HY, Song DQ, Zhang HR, Li JT, Zhang K, Wang YT, Zhang HQ (2007) Anal Chim Acta 589:239–246. doi:10.1016/j.aca.2007.03.003
18. Barriada-Pereira M, González-Castro MJ, Muniategui-Lorenzo S, López-Mahía P, Prada-Rodríguez D, Fernández-Fernández E (2007) Talanta 71:1345–1351. doi:10.1016/j.talanta.2006.07.012
19. Gonçalves C, Carvalho JJ, Azenha MA, Alpendurada MF (2006) J Chromatogr A 1110:6–14. doi:10.1016/j.chroma.2006.01.089
20. Richter BE, Ezzell JL, Felix D, Roberts KA, Later DW (1995) Am Lab 27:24–28
21. Moreno JLF, Liébanas FJA, Frenich AG, Vidal JLM (2006) J Chromatogr A 1111:97–105. doi:10.1016/j.chroma.2006.01.108
22. Frenich AG, Vidal JLM, Sicilia ADC, Rodríguez MJG, Bolaños PP (2006) Anal Chim Acta 558:42–52. doi:10.1016/j.aca.2005.11.012
23. Fernandez-Alvarez M, Llompart M, Lamas JP, Lores M, Garcia-Jares C, Cela R, Dagnac T (2009) J Chromatogr A 1216:2832–2842. doi:10.1016/j.chroma.2008.10.026
24. Presta MA, Kolberg DIS, Wickert C, Pizzutti IR, Adaime MB, Zanella R (2009) Chromatographia 69:237–241. doi:10.1365/s10337-008-0896-8
25. Hayward DG, Wong JW (2009) Anal Chem 81:5716–5723. doi:10.1021/ac900494a

26. Pawliszyn J (2003) Anal Chem 75:2543–2558. doi:10.1021/ac034094h
27. Iglesias-García I, Barriada-Pereira M, González-Castro MJ, Muniategui-Lorenzo S, López-Mahía P, Prada-Rodríguez D (2008) Anal Bioanal Chem 391:745–752. doi:10.1007/s00216-008-1914-2
28. Barriada-Pereira M, González-Castro MJ, Muniategui-Lorenzo S, López-Mahía P, Prada-Rodríguez D, Fernández-Fernández E (2004) J Chromatogr A 1061:133–139. doi:10.1016/j.chroma.2004.10.081
29. Shimelis O, Yang YH, Stenerson K, Kaneko T, Ye M (2007) J Chromatogr A 1165:18–25. doi:10.1016/j.chroma.2007.07.037