Talanta 81 (2010) 136–141

Contents lists available at ScienceDirect

Talanta

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

Determination of pyrethroid insecticides in sediment by gas chromatography—Ion trap tandem mass spectrometry

Jing You [a], Dongli Wang [b], Michael J. Lydy [b,*]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] Fisheries and Illinois Aquaculture Center and Department of Zoology, 171 Life Science II, Southern Illinois University, Carbondale, IL 62901, USA

ARTICLE INFO

Article history:
Received 31 October 2009
Received in revised form
18 November 2009
Accepted 19 November 2009
Available online 5 December 2009

Keywords:
Pyrethroid insecticides
Sediment
Gas chromatography-ion trap tandem mass spectrometry

ABSTRACT

A method was developed to analyze 10 pyrethroid insecticides in sediment by gas chromatography-ion trap tandem mass spectrometry (GC–MS/MS) after accelerated solvent extraction and solid phase extraction cleanup. The MS/MS parameters included selection of the precursor and product ions, excitation mode, excitation amplitude and the stability parameter q_z, and were optimized to maximize detection sensitivity. Due to its superior ability to remove background noise, GC–MS/MS showed elevated selectivity and improved confidence in peak identification compared to GC-electron capture detector (ECD). The instrumental detection limits for GC–MS/MS ranged from 148 to 4033 fg, and the calibration curves were linear from 5 to 1000 μg/L for all of the pyrethroids except cyfluthrin. The method detection limits for pyrethroids ranged from 0.10 to 0.80 μg/kg dry sediment, while the recoveries were 59.7–128%, 60.6–90.9% and 63.2–83.6% with the relative standard deviations of 5.3–25.3%, 1.1–10.6% and 3.0–15.6% at the spiking levels of 1, 5 and 20 μg/kg, respectively. Field sediment collected from California was used to validate the newly developed method, and analytical results were comparable to those by GC-ECD in most cases. However, as the result of a cleaner background, more pyrethroids were identified by GC–MS/MS.

1. Introduction

Pyrethroids are highly toxic to aquatic species and readily bind to sediment, and their application has been directly related to the reduction of benthic populations in both agricultural and urban areas [1–4]. A recent statewide study on sediment toxicity of urban creeks in California showed pyrethroids were the major culprit for toxicity to a benthic amphipod *Hyalella azteca* [5]. As a result there is an emerging need for a better understanding of the environmental fate and effects of pyrethroid residues in aquatic systems. However, studies examining the impacts of pyrethroids have been limited due to a lack of effective analytical methods. Toxicity of pyrethroids to sensitive species may exist at field sites where pyrethroids concentrations are barely detectable or not detected at all by currently used analytical techniques. In sediment with 1% organic carbon, most pyrethroids caused 50% mortality to *H. azteca* in a 10-d exposure at concentrations in the range of 4–10 ng/g and growth impairment at about half of these concentrations [1,6,7]. Moreover, the co-existence of multiple environmental stressors in sediment may cause toxicity to aquatic organisms at even lower concentrations than the toxic concentration of the individual compounds. Therefore, research on the mixture effects of pyrethroids may also be significantly hindered by the lack of sensitive analytical methods.

Gas chromatography (GC) coupled with electron capture detector (ECD) [8–11], or mass spectrometer (MS) [12–17] has been used to analyze trace pyrethroid residues in sediment. Although GC/MS provides structural information of the analytes for more accurate identification, it was less sensitive and had difficulty in detecting pyrethroids at low toxicologically relevant concentrations. On the other hand, GC-ECD showed better sensitivity, but positive errors may occur due to the complexity of sediment matrices even with dual-column confirmation. Use of multiple cleanup steps to remove co-extracted interference improved selectivity for GC-ECD analysis [9]; however, the laborious sample preparation procedures limited the applications of an analytical method to environmental monitoring which commonly involves processing a large number of samples. Therefore, it is critical to develop sensitive and selective methods to detect pyrethroids in complicated sediment matrices to protect benthic species with pyrethroid sensitivities comparable to *H. azteca*.

Due to its superior ability to remove background noise, tandem MS technique (GC–MS/MS), in which the selected precursor ions were subjected to a second MS analysis, could provide higher signal-noise ratios for the target analytes, resulting in higher selectivity, and lower detection limits compared to the traditional ECD and MS detectors [18]. At the same time, structural information could be obtained by monitoring the transition from the precursor

* Corresponding author. Tel.: +1 618 453 4091; fax: +1 618 453 6095.
E-mail address: mlydy@siu.edu (M.J. Lydy).

0039-9140/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2009.11.050

ion to the characteristic product ions in GC–MS, thus greater confidence for analyte identification can be achieved. Both precursor and product ions were within a single ion trap (IT) in ITMS, resulting in lower transport losses and instrumental costs. Thus, GC–MS/MS with ITMS instrumentation has been proposed to analyze trace pesticides, but the majority of these methods have focused on biological samples [19–25].

The objective of the present study was to develop an analytical method for pyrethroid residues in sediment by GC–MS/MS after accelerated solvent extraction (ASE), and solid phase extraction (SPE) cleanup. Parameters affecting MS/MS detection were optimized to achieve the best sensitivity and selectivity for individual pyrethroids, and the developed ASE-SPE-GC–MS/MS method was validated with both laboratory-spiked and field-collected sediment samples.

2. Material and methods

2.1. Chemicals and materials

Ten pyrethroid insecticides were analyzed in the present study, including bifenthrin, lambda-cyhalothrin, cypermethrin, cyfluthrin, deltamethrin, esfenvalerate, fenpropathrin, permethrin, resmethrin and tefluthrin. Their molecular weights are listed in Table 1. These insecticides were selected due to their heavy use in California where pyrethroids were identified as one of the major sources of sediment contamination [3–5]. Pyrethroid standards were purchased from ChemService Inc. (West Chester, PA, USA) and had purities >98%, and stock solutions (2.0 mg/ml) were made by diluting each pyrethroid into hexane. Decachlorobiphenyl (DCBP) and 4,4′-dibromoocta-fluorobiphenyl (DBOFB) were purchased from Supelco, added to the sediment before extraction, and used as surrogates to verify the performance of the analytical process. d^{14}-*p*-terphenyl was purchased from Supelco, added to the final extracts before instrumental analysis, and used as the internal standard (IS).

Sea sand, anhydrous Na_2SO_4, acetic acid, hexane, acetone, and dichloromethane were purchased from Fisher Scientific (Pittsburgh, PA, USA), and all solvents were pesticide grade. Copper powder was obtained from Resprep (Bellefonte, PA, USA). Prior to use, sea sand was washed with distilled water, and acetone sequentially and dried at 200 °C, while anhydrous Na_2SO_4 was baked at 450 °C for 4 h. Solid phase extraction (SPE) dual-layer cartridges packed with 600 mg primary/secondary amine (PSA) and 300 mg graphite carbon black (GCB) were from Supelco (Bellefonte, PA, USA).

2.2. Sediment spiking and collection

The sediment used in the present study was collected from the Touch of Nature Environmental Center in Carbondale, Illinois, USA. The sediment had a total organic carbon (TOC) content of $0.97 \pm 0.1\%$, and TOC was measured using an EA 1110 carbon-hydrogen-nitrogen elemental analyzer (CE Instruments, Milan, Italy) after removing carbonates by treating with 3 mol/L HCl. Previous chemical analyses and bioassays indicated that the control sediment contained no detectable pyrethroids, and showed no toxicity to *H. azteca*. Spiked sediment samples were prepared by adding an appropriate amount of a standard mixture of pyrethroids into the control sediment at 1, 5 and 20 μg/kg (dry weight, dw) with acetone as a carrier. The spiked sediment was thoroughly mixed with an overhead paddle for >1 h, and stored at 4 °C for 6 h prior to extraction.

Four field sediment samples were collected from central California, USA. Sample A was taken from Del Puerto Creek, which is an agriculture-influenced creek near Patterson, CA. Sample B was collected from an unnamed agricultural drain near Turlock, CA. Sample C was taken from Cottonwood Creek, an agriculture-influenced creek east of Madera CA. Finally, sample D was collected from a sump receiving urban runoff in Stockton, CA. The upper 1–2 cm of the sediment column was collected with a stainless steel scoop from the bank, and held on ice until returned to the laboratory. After being fully mixed, sediments were sieved through a 1 mm sieve, and held at −20 °C until analysis.

2.3. Sediment extraction and cleanup

Before extraction, frozen sediments were thawed, centrifuged to remove excess water, and dried overnight at approximately −48 °C and 0.133 psi using a FreeZone 2.5 Labconco freeze-drier (Kansas City, MO, USA). Matrix dispersive ASE and SPE were used for sediment extraction and cleanup, respectively, and followed previously validated procedures [9]. In brief, after homogenization, 5 g of dried sediment was mixed with 10 g of anhydrous Na_2SO_4, and 10 g cleaned sand, transferred into an extraction cell, and extracted with a mixture of acetone and dichloromethane (1:1, v/v) at 100 °C, and 2000 psi for two static cycles of 5 min using a Dionex 200 ASE (Sunnyvale, CA, USA). Surrogates were added to each sample before extraction.

The extract was concentrated, and solvent exchanged to 1 ml of hexane using a TurboVap II evaporator (Zymark, Hopkinton, MA, USA), and a Pierce Model 1878 Reactivap™ (Rockford, IL, USA). The concentrated extract was loaded onto a PSA/GCB SPE

Table 1
Optimized gas chromatography-ion trap tandem mass spectrometry method parameters.

Compounds	Molecular weight	Precursor ion (*m*/*z*)	Product ions (*m*/*z*)	ESL[a] (*m*/*z*)	Non-resonant EA[b] (V)
DBOFB[c]	455.9	456	227	201.3	2.60 resonant
Tefluthrin	418.7	177	127	77.9	85.0
p-Terphenyl-d^{14}[d]	244.4	245	226 + 242	108.0	0.75 resonant
Resmethrin	338.4	171	128 + 143	65.8	52.5
Bifenthrin	422.9	181	165	69.7	70.0
Fenpropathrin	349.4	181	152	79.7	90.0
Lambda-cyhalothrin	449.9	181	152	79.7	95.0
Permethrin	391.2	183	152 + 165 + 181	80.5	80.0
Cyfluthrin	434.3	226	199 + 206	55.8	0.80 resonant
Cypermethrin	416.3	181	152	79.7	92
DCBP[e]	498.7	498	426 + 428 + 430	219.9	2.60 resonant
Esfenvalerate	419.9	225	119 + 147	99.1	75.0
Deltamethrin	505.2	253	172:174	97.5	66.0

[a] ESL, excitation storage level representing the stability parameter (q_z).
[b] EA, excitation amplitude.
[c] DBOFB, 4,4′-dibromoocta-fluorobiphenyl, surrogate.
[d] *p*-Terphenyl-d^{14}, internal standard.
[e] DCBP, decachlorobiphenyl, surrogate.

cartridge which was capped with 1 cm anhydrous Na_2SO_4, and pre-washed with 3 ml of hexane. Target compounds were eluted from the cartridge with 7 ml of 30% dichloromethane in hexane mixture, concentrated and solvent exchanged to 0.1% acetic acid acidified hexane [26]. Sulfur interference was removed by shaking the effluent with granular copper.

2.4. Instrumental analytical method development

The cleaned extracts were analyzed using a Varian 3800 Saturn 2200 GC–MS/MS (Varian, Walnut Creek, CA, USA), and separation of analytes was achieved using a 30 m DB-5MS column with 0.25 mm i.d., and 0.25 μm film thickness. A 2 μl sample was injected in splitless mode at 260 °C with a CP-8410 autosampler, and the purge valve was turned on 2 min after injection. Helium was employed as the carrier gas at a flow-rate of 1.0 ml/min. The oven was set at 100 °C, heated to 200 °C at 8 °C/min, to 212 °C at 3 °C/min, to 250 °C at 8 °C/min, to 255 °C at 1 °C/min, then to 280 °C at 3 °C/min, and held at 280 °C for 3 min.

The identification and quantification of target pyrethroids were performed in MS/MS mode after electron impact (EI) ionization at an emission current of 30 μA, and data were analyzed with Saturn WS V. 6.41 software (Varian). The temperatures for the IT, manifold, and transfer line were 240, 100 and 290 °C, respectively. The analyses were conducted with a filament delay of 7 min, and under automatic gain control (AGC) with target values of 20,000 and 5000 for GC–MS and GC–MS/MS, respectively. Ion trap tests and mass calibration were conducted weekly with perfluorotributylamine.

To maximize sensitivity for the analytes in MS/MS operation, various parameters affecting collision induced dissociation efficiency (CID) were optimized, including the choice of the precursor and product ions, excitation amplitude (EA), and the stability parameter (q_z). Before MS/MS method development, the chromatographic segments for the target compounds were established based on their retention times in full scan mode. Then, from the full scan GC/MS spectra, the most abundant ion or fragment ion with a higher m/z and higher intensity of each compound was selected as the precursor ion, and subjected to further CID in a non-resonant excitation mode for MS/MS analysis. The automated method development (AMD) tool in the software was used to optimize EA. With a q_z of 0.4, the EA was calculated using three injections of a standard solution of a mixture of analytes at 100 μg/L. In the first injection, EA increased from 10 to 100 V at an interval of 10 V, and then EA varied within narrow ranges for each compound with intervals of 5 and 3 V in the second and third injections, respectively. The q_z was related to the broadband multi-frequency waveform used to isolate the precursor ion, and was expressed as an excitation storage level (ESL) in the software. Under the optimal EA for the precursor ions, a set of q_z values from 0.2 to 0.5 was tested to obtain the greatest intensity for the product ions. In addition, the mass defect (−50, 0 and +50 mmμ/100 μ), multiplier offset (100, 200 and 250 V), and mass range of the scanned ions were evaluated to maximize the pyrethroid signals as well.

2.5. Instrumental performance and method validation

Instrumental performance was evaluated by estimating the range, and linearity of the calibration curve, and instrument detection limits (IDL) were determined for each analyte by injection of pyrethroid mixtures in pure solution. Qualitative identity was established by comparing the similarity of the MS/MS spectrum of the peak within the retention time window to that of the corresponding standard. Eight calibration standard solutions were made by dissolving 5, 10, 25, 50, 100, 250, 500 and 1000 μg/L of each of pesticide and surrogate in acetic acid acidified hexane, while the IS was kept constant at 100 μg/L for all levels. Relative response factors (RRFs) were determined from the peak areas and concentrations of target analytes, and IS from the calibration curves, and the pyrethroids in the unknown samples were quantified using the internal calibration method. The linearity of the calibration curve was expressed as a regression coefficient r^2, and relative standard deviation (RSD) of RRF. The IDL was the concentration that provided a signal corresponding to three times noise, and was calculated from noise and the slope of the calibration curve using the equation (IDL = 3 noise/slope).

Pyrethroid residues in sediment were also analyzed with the newly developed GC–MS/MS method after ASE and SPE cleanup. The validation process included analyzing pyrethroids at different concentrations in laboratory-spiked and field-collected sediments. The method detection limit (MDL), accuracy and precision for each pyrethroid were evaluated, and analytical results of pyrethroids in the field-collected sediments were compared to those obtained by GC-ECD analysis [9]. The MDL is defined as the minimum concentration of a substance that can be measured with 99% confidence that the analyte concentration is greater than zero [27]. Sediment spiked with each pyrethroid at 1 μg/kg dw was extracted, cleaned, and analyzed in seven replicates, and MDL was calculated as follows: $MDL = st_{(0.99,\, n-1)}$, where s was the standard deviation of the seven replicate measurements, and $t_{(0.99,\, n-1)} = 3.14$ was the t-distribution value taken at a confidence level of 0.99 and degrees of freedom of six following the Code of Federal Regulation [28]. Accuracy and precision were presented by average recovery and RSD of analytical results of four replicates.

3. Results and discussion

3.1. Optimization of MS/MS conditions

A GC–MS/MS method was developed in the present study for identification and quantification of trace pyrethroid concentrations in sediment. Prior to the optimization of MS/MS conditions, the retention time (t_R), and MS spectrum of each compound was obtained using GC-EI/MS in a full scan mode. Chromatographic segments were set according to the t_R windows for each analyte, and MS/MS conditions were optimized for each segment, respectively.

The elevated selectivity and sensitivity of the MS/MS process were a result of the combination of three steps, namely selection of the precursor ion, dissociation of the selected precursor ion (CID), and detection of the formed product ions. The precursor ions were selected from the MS spectra of the analytes obtained with an EI source at an emission current of 30 μA. The hard ionization by the EI source caused extensive fragmentation, and intensity of the molecular ions were low. Hence, the most abundant fragment ions were selected as the precursor ions for most pyrethroids except for the pyrethroids whose base ions had low m/z. In this case, the less fragmented ions with relatively high intensity were chosen. The selected precursor ions were reported in Table 1.

After exclusion of other matrix ions, the isolated precursor ions were further excited, and dissociated to the product ions inside the IT. The effectiveness of the CID process directly limited abundance of the product ions, in turn, the detection sensitivity of the MS/MS method. Therefore, parameters that influenced CID were optimized to maximize the yields of the product ions. The parameters included excitation mode, EA, q_z in the form of ESL, mass defect, and mass range of the scanned ions. Bauerle et al. [20] reported that when IDLs were similar, a slightly higher signal-to-noise ratio (S/N) was achieved by using the non-resonant excitation mode compared to resonant excitation for pyrethroids analyzed by GC-chemical ionization-MS/MS. The non-resonant excitation protocol was also employed by Béguin et al. [18], and they claimed that this mode provided more spectra information of the product ions through

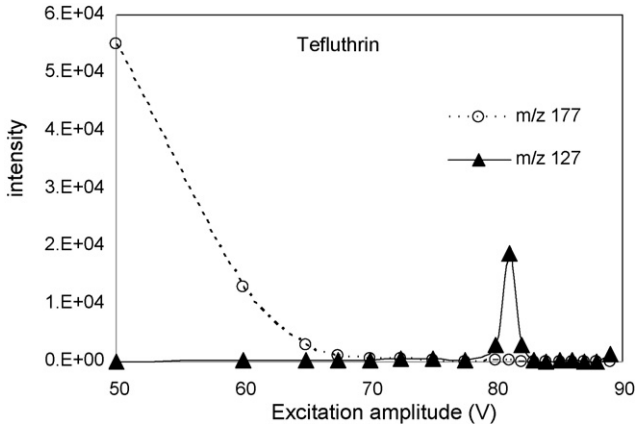

Fig. 1. Influence of excitation amplitude on the intensity of the precursor ion (m/z 177), and the product ion (m/z 127) of tefluthrin in the collision induced dissociation process.

consecutive dissociation, and enhanced S/N through better control of energy transfer. Therefore, non-resonant excitation mode was applied for the target pyrethroids in the present study with the exception of cyfluthrin for which a baseline jump was encountered. Hence a more selective resonant excitation mode was used for cyfluthrin, as well as the surrogates, and the IS (Table 1).

After CID, the most predominant product ions were chosen for quantification as shown in Table 1. For a greater production of the product ions, the AMD tool was used to optimize EA. With the increase of EA, the intensity of the precursor ions decreased to nearly zero, while the intensity of the product ions increased until reaching a maximum, and then decreased. The profiles of intensity of the precursor ion (m/z 177), and the product ion (m/z 127) of tefluthrin with the change of EA are shown in Fig. 1. The increase in the abundance of the product ions when EA was less than 85 V was contributed to increased CID efficiency, while the reduction of product ions with the continuous increase in EA might be the result of the lack of the precursor ions left in the IT. Therefore, 85 V was chosen as the EA for tefluthrin, and the optimized EAs for all of the compounds are listed in Table 1. At the selected EA for each compound, q_z was optimized by several injections of standard mixtures with q_z values set from 0.2 to 0.5. As shown in Fig. 2, the intensity of the product ions increased when q_z increased, and the maximum was reached when q_z equaled 0.35 for resmethrin, bifenthrin, and deltamethrin, and 0.4 for the remaining pyrethroids. The ESL values corresponding to the optimized q_z are reported in Table 1. Other than the two main factors (EA and q_z), the effects of

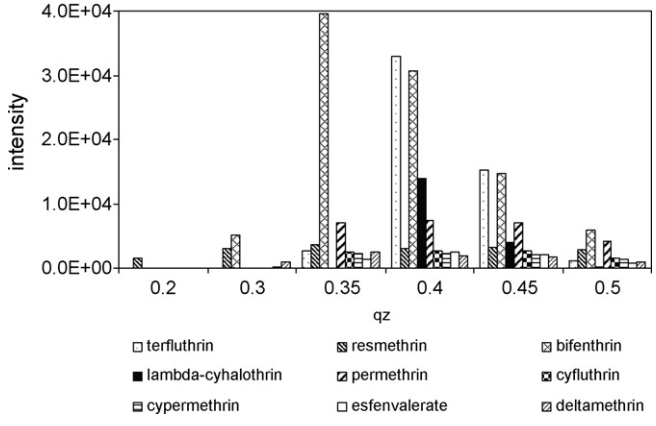

Fig. 2. Influence of stability parameter (q_z) on the intensity of the product ion of each pyrethroid in the collision induced dissociation process.

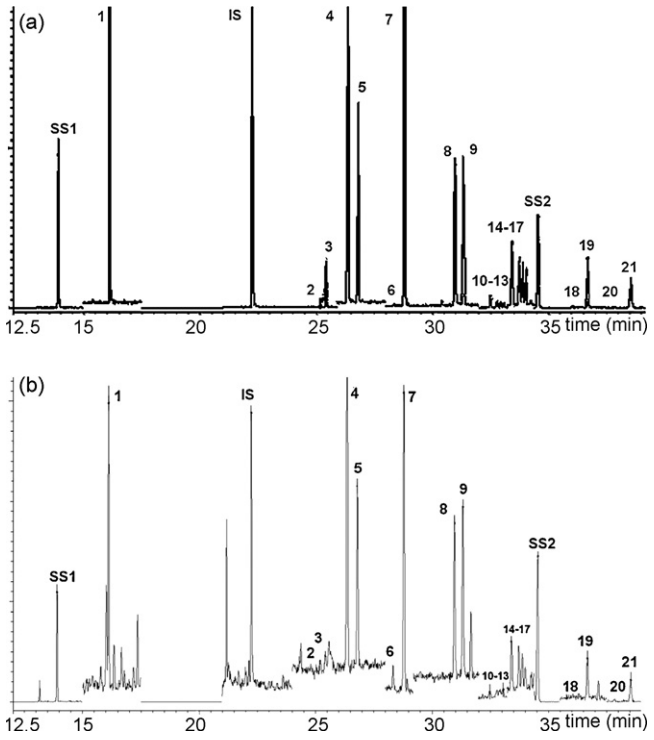

Fig. 3. Total ion chromatograms of pyrethroids, internal standard (IS) and surrogates (SS) in a standard solution at 100 μg/L (a), and in sediment spiked at 5 μg/kg dry weight (b) analyzed by gas chromatography-ion trap tandem mass spectrometry. Peaks: 1—tefluthrin; 2 and 3—resmethrin 1 and 2; 4—bifenthrin; 5—fenpropathrin; 6 and 7—lambda-cyhalothrin 1 and 2; 8 and 9—permethrin 1 and 2; 10–13—cyfluthrin 1–4; 14–17—cypermethrin 1–4; 18 and 19—esfenvalerate 1 and 2; 20 and 21—deltamethrin 1 and 2; SS1—4,4′-dibromooctaflurobiphenyl; SS2—decachlorobiphenyl; IS—*p*-terphenyl-d ^{14}.

mass defect, multiplier offset, and mass range of the scanned ions on the intensity of the product ions were also investigated. Results showed a mass defect of −50 mmμ/100 μ worked best for all compounds except of esfenvalerate, and DCBP for which a mass defect of +50 mmμ/100 μ provided the most product ions. Intensity of the product ions increased with the increase in multiplier offset, so the highest tested value of 250 V was applied. The narrower the mass range of scanned ions, the better detection sensitivity. Thus, the mass range of scanned ions was set to the narrowest setting, but still included all the product ions used for quantification.

3.2. Instrumental performance of GC–MS/MS

The instrumental performance was validated by the IDL calculation and the calibration linearity of pyrethroid standards in pure solution. The calibration standards were analyzed with the optimized GC–MS/MS method (Table 1). Because of the existence of isomers, multiple peaks were observed for several pyrethroids as shown in Fig. 3a, which represented the total ion chromatogram (TIC) of the analytes at 100 μg/L. As shown in Table 2, the calibration curves were linear with r^2 of 0.9971–0.9999, and the linearity ranged from 5 to 1000 μg/L for all pyrethroids except for cyfluthrin (25–1000 μg/L). The RSDs of RRFs for pyrethroids to the IS, *p*-terphenyl-d^{14} were 5.8–11.9%, indicating good linearity and repeatability of the developed method. The IDLs were defined as the concentrations producing a S/N of 3, and ranged from 148 to 4033 fg (for 2 μl of injected volume) corresponding to 0.074–2.02 μg/L in solution. Cyfluthrin had the highest IDLs, and this might be explained by the presence of four isomers, and a different CID mode.

Table 2
Range and correlation coefficients (r^2) of the calibration curves, and instrumental detection limits (IDL), and method detection limits (MDL) for pyrethroids in solution or sediment analyzed by gas chromatography-ion trap tandem mass spectrometry after accelerated solvent extraction and solid phase extraction cleanup.

	Range (μg/L)	r^2	IDL (fg)	MDL (μg/kg dry weight)
Tefluthrin	5–1000	0.9971	148	0.10
Resmethrin	5–1000	0.9999	2885	0.49
Bifenthrin	5–1000	0.9981	438	0.63
Fenpropathrin	5–1000	0.9994	575	0.66
Lambda-cyhalothrin	5–1000	0.9991	479	0.54
Permethrin	5–1000	0.9996	716	0.57
Cyfluthrin	25–1000	0.9996	4033	0.80
Cypermethrin	5–1000	0.9999	2523	0.42
Esfenvalerate	5–1000	0.9979	1286	0.50
Deltamethrin	5–1000	0.9996	1250	0.53

3.3. Method validation with laboratory-spiked sediments

Matrix interference can dramatically affect detection of trace analytes. In order to assess the capability of the GC–MS/MS method to analyze pyrethroids in sediment, pyrethroids were spiked into control sediment at various concentrations, and then quantified using GC–MS/MS after ASE extraction and SPE cleanup [9]. Fig. 3b showed the TIC of the GC–MS/MS analysis of sediment spiked at 5 μg/kg dw. The matrix interference was minimal, and the detection based on the selected product ion further reduced interference, and baseline noise.

Different from the IDL, which was estimated by injecting pure solution, the MDLs represented the sensitivity of the whole analytical procedure including sample preparation, and instrumental identification and quantification. The MDLs were calculated from the standard deviation of seven replicates of sediment samples spiked at 1 μg/kg dw. As shown in Table 2, all the MDLs were less than 1 μg/kg dw, and comparable to those analyzed by GC-ECD [8,9], or GC-high resolution MS [16].

Table 3 summarized the mean recoveries of the spiked pyrethroids at three concentrations, and recoveries ranged from 59.7% to 128%, from 60.6% to 90.9%, and from 63.2% to 83.6% for sediment spiked at 1, 5 and 20 μg/kg dw, respectively. The RSD was generally used to characterize the reproducibility of an analytical method. As shown in Table 3, the RSDs were 5.3–25.3%, 1.1–10.6% and 3.0–15.6% for all pyrethroids at the spiking levels of 1, 5 and 20 μg/kg dw, respectively.

3.4. Method application in field-contaminated sediment

Sediment samples collected from California were quantified using the newly developed GC–MS/MS, and a previously developed GC-ECD method [9] after ASE extraction, and SPE cleanup. The comparison of the analytical results is presented in Table 4, and the chromatograms of sediment B analyzed by the two techniques are shown in Fig. 4. Cleaner chromatograms were obtained

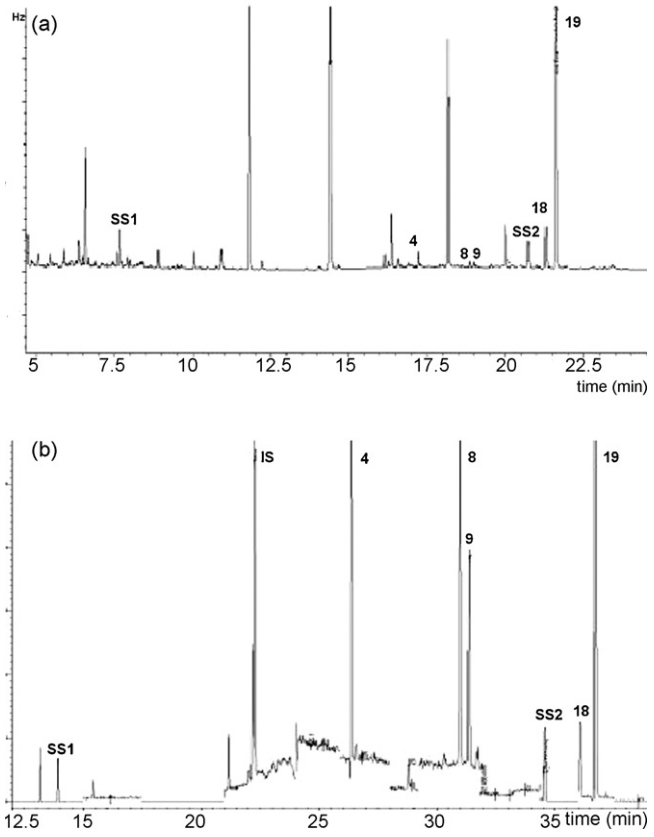

Fig. 4. Chromatograms of pyrethroids in field – collected sediment B by gas chromatography – electron capture detection (a) and gas chromatography-ion trap tandem mass spectrometry (total ion chromatogram) (b). Peak numbers are the same as those in Fig. 3.

Table 3
Mean recovery (%) and relative standard deviation (RSD, %) of various concentrations of pyrethroids in laboratory-spiked sediments analyzed by gas chromatography-ion trap tandem mass spectrometry after accelerated solvent extraction and solid phase extraction cleanup.

	1 μg/kg (n = 7)		5 μg/kg (n = 4)		20 μg/kg (n = 4)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Tefluthrin	59.7	5.3	61.4	2.3	63.2	15.6
Resmethrin	94.7	16.4	72.4	10.6	73.1	13.8
Bifenthrin	110	18.4	86.4	1.6	83.6	10.1
Fenpropathrin	98.2	21.4	82.6	1.1	78.7	9.3
Lambda-cyhalothrin	117	14.7	86.7	5.2	75.4	7.5
Permethrin	128	14.2	90.9	3.6	82.6	13.3
Cyfluthrin	101	25.3	79.6	1.7	75.4	3.0
Cypermethrin	97.2	13.7	64.6	2.9	72.0	13.2
Esfenvalerate	105	15.3	67.4	2.6	63.7	7.4
Deltamethrin	91.2	18.4	60.6	8.2	67.9	11.6

Table 4
Pyrethroid concentrations (C_s, μg/kg dry weight) in field-contaminated sediments analyzed by gas chromatography-ion trap tandem mass spectrometry (MS/MS) and gas chromatography – electron capture detection (ECD) after accelerated solvent extraction and solid phase extraction cleanup.

Sediment	A		B		C		D	
	MS/MS	ECD	MS/MS	ECD	MS/MS	ECD	MS/MS	ECD
Tefluthrin	nd	nd	nd	nd	nd	nd	1.1	nd
Resmethrin	nd	–	<RL	–	nd	–	nd	–
Bifenthrin	15.2	17.0	9.6	9.9	1.4	nd	318	405
Fenpropathrin	nd	nd	<RL	nd	<RL	nd	23.2	60.2
Lambda-cyhalothrin	<RL	nd	<RL	<RL	1.6	nd	36.9	21.6
Permethrin	1.4	<RL	17.7	10.8	151	126	152	109
Cyfluthrin	nd	nd	<RL	nd	<RL	2.4	138	70.0
Cypermethrin	<RL	nd	<RL	nd	nd	nd	37.4	35.5
Esfenvalerate	nd	<RL	109	203	1.6	<RL	30.4	29.8
Deltamethrin	nd	nd	nd	nd	nd	1.0	1.1	nd

nd, not detected; –, no signal; <RL, less than the reporting limit of 1 μg/kg dry weight.

using GC–MS/MS, and the results matched well for the two methods in most cases. However, differences in results did exist, and may be attributed to the matrix response enhancement effect, and/or interference by various matrix components.

Bifenthrin and permethrin were the most frequently detected pyrethroids, and were identified by GC–MS/MS in all field-collected sediments. Deltamethrin was detected at concentrations close to the RL in sample C by GC-ECD and sample D by GC–MS/MS. It has been reported that tralomethrin would undergo debromination to form deltamethrin in the GC inlet [29], thus the detected deltamethrin in the field samples may be tralomethrin and/or deltamethrin. Overall, the GC–MS/MS method provided a slightly better identification of the pyrethroids from the complicated matrices in comparisons to GC-ECD, especially at low concentrations. Several pyrethroids were detected using the GC–MS/MS, and were not detected using GC-ECD, and this may be attributed to the difficulty in differentiating trace pyrethroids from the matrix interference. Using the spectrum as confirmation, GC–MS/MS provided more confidence in peak identification than GC-ECD. Another advantage of MS/MS was its ability to analyze pyrethroids without electron capture elements, such as resmethrin, which produced no signal with ECD. As shown in Table 4, trace resmethrin was identified by GC–MS/MS in sample B, though the concentration was below the reporting limit. Thus, more pyrethroids were identified and quantified using the GC–MS/MS technique.

4. Conclusions

Using GC–MS/MS to identify and quantify trace pyrethroids in sediment extracts after ASE extraction and SPE cleanup greatly reduced potential matrix interference, provided higher confidence in analyte identification with confirmation information from the MS/MS spectrum, improved method selectivity, and more pyrethroids were identified and quantified compared to GC-ECD.

Acknowledgements

Jing You was supported by the "Hundred Talents" Program of the Chinese Academy of Sciences (kzcx2-yw-BR-05), and this support was greatly appreciated. The authors wish to thank D. Weston and R. Kelley for sediment sample collection and processing. GIGCAS contribution number 1146.

References

[1] E.L. Amweg, D.P. Weston, N.M. Ureda, Environ. Toxicol. Chem. 24 (2005) 966–972.
[2] E.L. Amweg, D.P. Weston, J. You, M.J. Lydy, Environ. Sci. Technol. 40 (2006) 1700–1706.
[3] D.P. Weston, R.W. Holmes, J. You, M.J. Lydy, Environ. Sci. Technol. 39 (2005) 9778–9784.
[4] D.P. Weston, J. You, M.J. Lydy, Environ. Sci. Technol. 38 (2004) 2752–2759.
[5] R.W. Holmes, B.S. Anderson, B.M. Phillips, J.W. Hunt, D.B. Crane, A. Mekebri, V. Connor, Environ. Sci. Technol. 42 (2008) 7003–7009.
[6] J.D. Maul, A.J. Trimble, M.J. Lydy, Environ. Toxicol. Chem. 27 (2008) 945–952.
[7] S.J. Maund, M.J. Hamer, M.C.G. Lane, E. Farrelly, J.H. Rapley, U.M. Goggin, W.E. Gentle, Environ. Toxicol. Chem. 21 (2002) 9–15.
[8] J. You, D.P. Weston, M.J. Lydy, Arch. Environ. Contam. Toxicol. 47 (2004) 141–147.
[9] J. You, D.P. Weston, M.J. Lydy, ACS Sym. Ser. 991 (2008) 87–113.
[10] E. Bennett, M. Moore, C. Cooper, S.J. Smith, Bull. Environ. Contam. Toxicol. 64 (2000) 825–833.
[11] A. Mekebri, D.B. Crane, G.J. Blondina, D.R. Oros, J.L. Rocca, Bull. Environ. Contam. Toxicol. 80 (2008) 455–460.
[12] G.A. Bonwick, C. Sunb, P. Abdul-Latif, P.J. Baugh, C.J. Smith, R. Armitaged, D.H. Davies, J. Chromatogr. A 707 (1995) 293.
[13] P.M. Hancock, M. Yasin, P.J. Baugh, G.A. Bonwick, D.H. Davies, Int. J. Environ. Anal. Chem. 67 (1997) 81–95.
[14] K. Miranda, M. Cunha, E. Dores, D. Calheiros, J. Environ. Sci. Health B 43 (2008) 717–722.
[15] K.L. Smalling, K.M. Kuivila, J. Chromatogr. A 1210 (2008) 8–18.
[16] M.B. Woudneh, D.R. Oros, J. Chromatogr. A 1135 (2006) 71–77.
[17] M. Yasin, P.J. Baugh, G.A. Bonwick, D.H. Davies, P. Hancock, M. Leinoudi, J. Chromatogr. A 754 (1996) 235–243.
[18] S. Béguin, A. Jadas-Hécart, J.-C. Tabet, P.-Y. Communal, J. Mass Spectrom. 41 (2006) 1304–1314.
[19] F.J. Arrebola, J.L.M. Vidal, M. Mateu-Sánchez, F.J. Álvarez-Castellón, Anal. Chim. Acta 484 (2003) 167–180.
[20] G.F. Bauerle, K.L. Ray, J.S. Brodbelt, Anal. Chim. Acta 317 (1995) 137–148.
[21] F.A. Esteve-Turrillas, A. Pastor, M.D.L. Guardia, Anal. Chim. Acta 553 (2005) 50–57.
[22] A.G. Frenich, P. Plaza-Bolanos, J.L.M. Vidal, J. Chromatogr. A 1203 (2008) 229–238.
[23] D. Garcia-Rodriguez, A.M. Carro, R.A. Lorenzo, F. Fernandez, R. Cela, J. Sep. Sci. 31 (2008) 2882–2890.
[24] M. Mezcua, C. Ferrer, J.F. García-Reyes, M.J. Martínez-Bueno, M. Sigrist, A.R. Fernández-Alba, Food Chem. 112 (2009) 221–225.
[25] S. Walorczyk, J. Chromatogr. A 1208 (2008) 202–214.
[26] J. You, M.J. Lydy, J. Chromatogr. A 1166 (2007) 181–190.
[27] G. Collins, Environmental Monitoring and Assessment Program: Chemical Method Evaluation Guidance, EPA 620/R-96/001, US Environmental Protection Agency, Columbus, OH, 1996.
[28] U.S. Government, W.D.C (Ed.), Code of Federal Regulations (CFR) 40 Part 136, Appendix B, 1993, pp. 554–555.
[29] A. Valverde, A. Aquilera, M. Rodríguez, M. Boulaid, J. Chromatogr. A 943 (2002) 101–111.