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Journal of Chromatography A, 1098 (2005) 150–155
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of the limits of identification and quantitation of selected organochlorine and organophosphorous pesticide residues in surface water by full-scan gas chromatography/mass spectrometry

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Received 16 May 2005; received in revised form 7 August 2005; accepted 22 August 2005
Available online 8 September 2005

Abstract

In this work, we report a reliable method for quantitation and determination of the limits of identification of 14 organochlorine and organophosphorous pesticide (OPP) residues in surface water. The method features the simultaneous identification and quantitation of targeted pesticides and the possibility of identification of any other eluting compounds. The method is based on liquid–liquid extraction (LLE) with a mixture of petroleum ether and dichloromethane (70:30, v/v) followed by gas chromatographic separation and a full-scan mass spectrometric detection (GC–MS). The method presents a new validation parameter, limit of identification (LOI) which is defined for our purpose as the lowest analyte concentration that yields a library searchable mass spectrum. The method is linear over the range 0.048–1.20 $\mu g\,L^{-1}$ for nine pesticides and 0.024–0.60 $\mu g\,L^{-1}$ for the other five pesticides. Correlation coefficients vary between 0.988 and 0.998. Limits of detection (LODs) vary between 0.005 and 0.05 $\mu g\,L^{-1}$ for 4,4′-DDT and LOIs vary between 0.012 and 0.048 $\mu g\,L^{-1}$.

Keywords: Organochlorine pesticides; Organphosphorous pesticides; GC/MS; Surface water; Identification; Analysis

1. Introduction

Pesticide contamination of surface water and ground water from agricultural use has been a concern for a long time. Attention is usually focused on contamination by organochlorine pesticides (OCPs) due to their toxicity and persistence in environment; and contamination by common pesticides, such as organophosphorous pesticides (OPPs) due to misuse and runoffs [1–3].

There are extensive reported methods for monitoring pesticide residues in water, soil, food and feedstuff [4–8]. They are based on either liquid–liquid extraction (LLE) or solid-phase extraction (SPE), followed by gas chromatography (GC) or high performance liquid chromatography (HPLC) separations employing wide range of detectors. For GC separations, electron capture detector (ECD) and nitrogen phosphorous detector (NPD) are popular for detection of OCps and OPPs residues, respectively. Mass spectrometric detector (MS) is a universal detector and is employed for simultaneous determination of OCPs and OPPs residues. However, most methods employ MS in either the single ion-monitoring mode (SIM) for quadrapole detectors and single ion storage (SIS) for ion-trap detectors or MS/MS in which sensitivity is improved at expense of identification capabilities [9–12].

Confirmation of targeted analytes in conjunction with their detection and quantitation is a major concern, especially when legal or regulatory issues are involved [13–15]. Chromatographic methods with MS detection are capable of identifying analytes, however, the credibility of confirmation is based on the selected method. In the full-scan MS method, all ions produced in the MS are employed in confirmation and quantitation of the targeted analyte. High reliability of identification is achieved by the availability of standard MS libraries, such as the National Institute of Standards and Technology (NIST) library that contains more than one hundred and fifty thousand mass spectra of standard organic compounds [16]. The MS of targeted analyte

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doi:10.1016/j.chroma.2005.08.064

at the top of its chromatographic peak is fitted to the best matching compound in the library. Quantitation and identification by the SIM and MS/MS method is achieved by the selection of at least three major ions related to the targeted analyte, "three ion criteria" principle. One ion is assigned for quantitation and the other two ions are assigned for confirmation. The same "three ion criteria" principle is also applied for the MS/MS method, but one ion is the parent ion (from first MS) and the other two are selected from product ions (from second MS) [15].

The full-scan method is a standard feature in all MS detectors, however, most reported methods employ it for qualitative analysis only. A major advantage of the full-scan method over SIM method is the capability of simultaneous identification and quantitation of separated analytes and identification of other eluted compounds that could be of interest. A major disadvantage is that it is less sensitive; however, extreme sensitivities are not always required especially in quality control analysis, however, the full-scan method is still required to assign the detection and confirmation ions in the SIM and MS/MS methods. The baseline in full-scan method is noisier; however, it could be minimized by careful optimization of extraction method, selection of integrating mass range and the possibility of excluding some ions that are not related to targeted analytes. In full-scan MS method, limit of identification (LOI) which is defined for our purpose as the lowest analyte concentration that yields a library searchable mass spectrum could be determined and compared to other traditional statistical parameters, such as the limit of detection (LOD).

In this study, we report a reliable analytical method for monitoring 14 selected OCP and OPP residues in surface water employing the full-scan MS method. For the first time we present a realistic method for determining LOIs for targeted pesticides. GC parameters were optimized for baseline resolution between targeted pesticides themselves and internal standard. MS parameters were optimized for highest sensitivities combined with identification of targeted pesticides. Both conventional LLE and SPE methods were evaluated for highest recoveries and minimum extraction of endogenous compounds. The method was validated for linearity, reliability, recovery, LOIs and LODs. Finally, the method was applied for analyzing real surface water samples collected from different sites in Jordan.

2. Experimental

2.1. Reagents and chemicals

Selected pesticides: α-HCH, β-HCH, diazinon, malaxon, alachlor, fenitrothion, malathion, chloropyriphos, parathion, primiphosethyl (internal standard), endosulfan I, 4,4′-DDE, Endrin, Endosulfan II and 4,4′-DDT were obtained as a gift from the National Center of Agriculture Research and Technology Transfer (NCARTT) in Jordan, with purities larger than 98.5%. Organic solvents are pesticide grade (Pest Scan, Stillogran, Industrial park, Irland). Other chemicals are analytical grade (Sigma, St. Louis, MO, USA) and water was double distilled. Solid-phase extraction discs were Empore (3M, St. Paul, MN, USA) with a 47 mm diameter and 0.50 mm thickness of 90% octadecyl C18-bonded phase silica particles.

2.2. Apparatus

A Varian Saturn 2000 GC/MS/MS (Watnut Greek, CA, USA) ion trap mass detector was employed. It consists of a Varian CP-3800 gas chromatograph with a 1079 universal capillary injector and coupled with a Saturn 2000 mass spectrometer. The data system contains all the software required for calibration, collection of GC/MS spectra and data processing for qualitative and quantitative analysis. Also it contains a NIST library with more than one hundred and fifty thousand mass spectra for standard compounds.

Separations were performed by a DB-5.625 fused silica capillary column (Varian, Watnut Greek, CA, USA) coated with a 0.25 μm thickness of 5% phenyl–95% dimethyl polysiloxane, low bleed MS with a length of 30 m. The carrier gas was 99.999% helium at a flow rate of 0.7 mL min^{-1}. The injector temperature was set at 255 °C and 1.0 μL was injected in the split-less mode. Samples were analyzed using the following temperature programme: initial temperature 70 °C (held for 1 min), increased by 25 °C min^{-1} to 182 °C (held for 0.5 min), increased by 2 °C min^{-1} to 190 °C (held for 2 min), increased by 0.4 °C min^{-1} to 193 °C, increased by 15 °C to 217 °C and finally increased by 2 °C min^{-1} to 244 °C (held for 2 min). The MS was operated in the full-scan EI mode. The mass range was 50–410 U with a 0.75 s/scan. The manifold, trap and transfer line temperatures were set to 50, 200 and 250 °C, respectively. The emission current of the ionization filament was set to 10 μA generating electrons with 70 eV energy.

2.3. Calibration solutions

A stock solution containing nine pesticides at 2.0 μg mL^{-1} and five pesticides at 1.0 μg mL^{-1} in methanol was prepared from individual pesticide stock solutions. Also a 10.0 μg mL^{-1} of internal standard, primiphos-ethyl was prepared. Selection of two concentration ranges is to keep the intensities of the 14 pesticides in the GC/TIC–MS chromatogram comparable. Measured amounts of stock solution were spiked into 500 mL pesticide-free surface water samples to prepare eight concentrations in the range 0.048–1.20 μg L^{-1} for nine pesticides and 0.024–0.60 μg L^{-1} for other pesticides. Pesticide-free surface water was employed in calibration and validation studies to exclude further studies on matrix effects. This water was tested for absence of pesticides by GC/ECD for OCPs and GC/NPD for OPPs.

2.4. Sample collections

Thirty surface water samples were collected from different sites in Jordan. A 2.5-L volume of water was collected in glass bottles from each sampling site. After filling with water, the bottles were sealed with screw caps lined with aluminum foil. Samples were filtered through fiberglass filter to remove turbidity and debris; and stored at 4 °C prior to extraction.

2.5. Methodology

Optimization of GC and MS parameters was based on sequential injections of a 1.00 μL from calibration standards. GC parameters and MS parameters were optimized to obtain baseline separation between the studied pesticides and internal standard

For LLE, a 500-mL water sample as it is (for analysis) or spiked pesticide-free surface water sample (for optimization and validation studies) was transferred into a 1-L separatory funnel, then a 60 mL of the organic solvent was added. The separatory funnel was shacken vigorously for about four minutes with periodic venting to release excess pressure. The organic layer was allowed to separate for 10 min. and was collected into a 250-mL Erlenmeyer flask. A second 40 mL of the organic solvent was added and extraction procedure was repeated twice. The combined extract was percolated through an anhydrous sodium sulphate column. The dried extract was evaporated using rotary evaporator adjusted at 35 °C until the volume reached 2–3 mL. The final extract was transferred quantitatively by rinsing with 1 mL aliquots of the organic solvent into a concentrator tube. The combined extract was then evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved with 300 μL of *n*-hexane containing a 1.0 $\mu g\,mL^{-1}$ of primiphos-ethyl. One microliter was injected into the GC in the split-less mode.

For SPE, the membrane disc was conditioned by 20 mL of elution solvent followed by 10-mL methanol and two 10-mL portions of distilled water, taking into consideration keeping the disc wet. A 500-mL water sample as it is or spiked, was mixed with 2.5-mL methanol and passed through the disc in about 20 min, by adjusting the vacuum pressure. The retained compounds were washed with 30-mL double distilled water and eluted by 30 mL of elution solvent. The elution solvent was dried by sodium sulphate and evaporated using a rotary evaporator and nitrogen as explained in liquid–liquid extraction. One microliter was injected into the GC in the split-less mode.

2.6. Validation

Validation studies are based on pesticide concentrations in spiked pesticide-free surface water samples before extraction; that is 0.048–1.20 $\mu g\,L^{-1}$ for nine pesticides and 0.024–0.60 $\mu g\,L^{-1}$ for the other five.

LOI for each pesticide was determined experimentally by firstly selecting a full-scan GC–MS chromatogram of a spiked pesticide-free water sample with a relatively high concentration. The MS at the top of each peak is searched with NIST library with the best fit. Usually the best-matched 25 compounds are displayed. If the examined pesticide is displayed among the best five, it is considered library searchable at this concentration. Then another spiked sample with the next lower concentration is selected and the process is repeated. If the examined pesticide was not among the best five selected, we try to improve the search by changing the mass range and so on. Reported LOIs are accompanied with their library-search mass range. LOD for each pesticide was determined as the lowest concentration of a compound yielding a response with a signal-to noise ratio (S/N) of 3. LODs are calculated by the software of the instrument as follows: the standard deviation (SD) of the base line is calculated at points just before and after the elution of the compound, the value corresponding to 3 SD is calculated and converted to concentration units by using the fortified concentration of the compound.

Linearity of the method was demonstrated by running the final extracts of the spiked pesticide-free water samples in triplicates at eight spiking concentrations. Precision and accuracy studies were assessed in conjunction with linearity studies in triplicate employing three nominal concentrations for each pesticide. Accuracy is reported as percent bias and precision is reported as percent relative standard deviation (RSD).

Recoveries were assessed, by comparing chromatograms of calibration standards with final extracts of spiked samples with the same calibration standards. Measured concentrations for analyzed samples were determined by application of the appropriate calibration curve (peak height ratio verses concentration) for each pesticide obtained from linear least squares method in each occasion.

3. Results

Method development will include optimization of GC and MS parameters, and extraction methods. Method evaluation will include statistical parameters and analysis of real samples.

3.1. Method development

Fig. 1 represents a typical full-scan GC–MS chromatogram for a spiked pesticide-free surface water sample extracted with

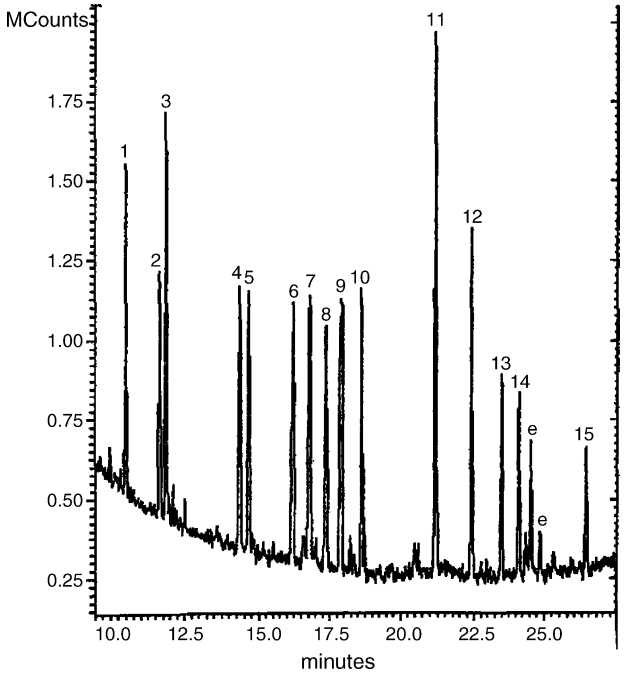

Fig. 1. A typical full-scan GC–MS chromatogram for a spiked pesticide-free surface water sample under optimized conditions at 1.20 $\mu g\,L^{-1}$ for nine pesticides and 0.60 $\mu g\,L^{-1}$ for the other pesticides. For peak assignments and concentrations refer to Table 1, e: endogenous.

a mixture of petroleum ether and dichloromethane (70:30, v/v). Pesticides were eluted between 186 and 244 °C. A temperature gradient of 2 °C/min was enough for baseline resolution of the first three peaks, while a lower gradient, 0.4 °C/min, was required for baseline resolution of peaks 4–10. The mass range was between 70 and 410 U to eliminate acquisition of most fragments coming from solvent at lower level and to include the molecular ion for the largest targeted pesticide, 405 U.

For optimization of LLE method; various organic solvents were evaluated. The full-scan GC–MS chromatograms from diethyl ether and ethyl acetate suffer from a very noisy baseline, ±200 kilo counts (kc) and co-elution of endogenous compounds that overlap with some pesticides, while that from dichloromethane shows a noisy baseline, ±150 kc, but with less endogenous compounds. The full-scan GC–MS chromatograms from petroleum ether shows a less noisy baseline, ±20 kc, however, some pesticides were poorly extracted. Most of endogenous compounds were identified as phthalate derived compounds. Thus, various binary mixtures were evaluated and best results were obtained with a mixture of petroleum ether and dichloromethane (70:30, v/v) as shown in Fig. 1.

Optimization of SPE method was limited to selection of best eluting solvent for adsorbed compounds. Various binary mixtures selected from petroleum ether, dichloromethane, ethyl acetate and diethyl ether, were evaluated; best results were obtained with a binary mixture of dichloromethane and ethyl acetate (90:10, v/v). A typical chromatogram is presented in Fig. 2.

By comparison between Figs. 1 and 2, and further recovery studies, we found that the SPE method suffers from a more noisy background, elution of more endogenous compounds and higher uncertainties of recovered spiked concentrations, which makes

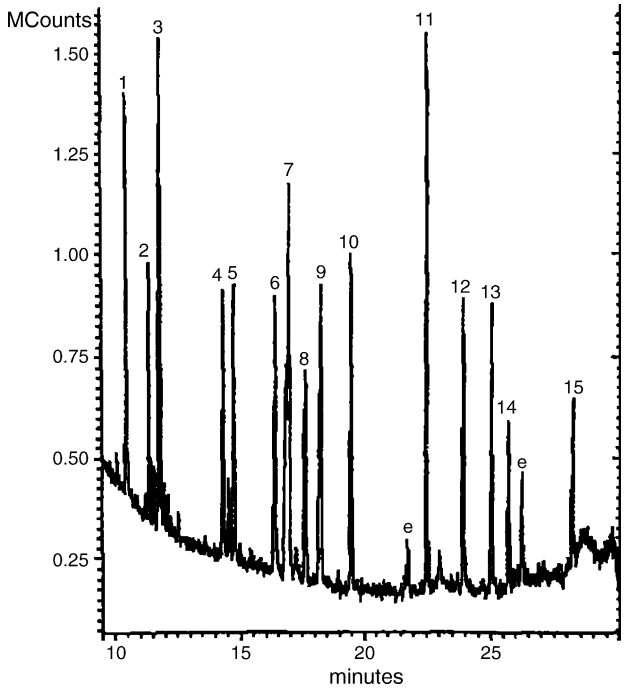

Fig. 2. Same as Fig. 1 but employing solid-phase extraction.

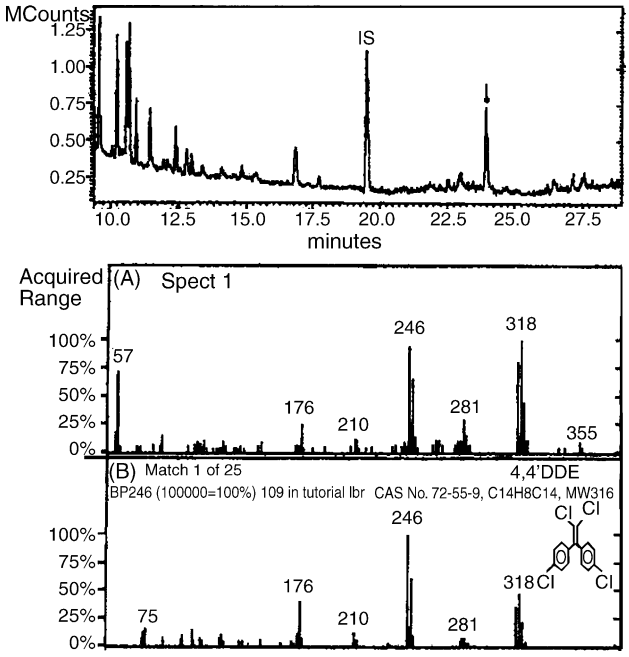

Fig. 3. "Upper" is a full-scan GC–MS for a real sample. (A) The MS at the top of the peak (↓) and (B) the NIST MS for 4,4′-DDE.

it less attractive for the full-scan MS method. Thus, LLE was preferred and employed in sequential studies.

3.2. Method evaluation

Statistical results including slope, intercept, LODs and LOIs are presented in Table 1. Uncertainties of slopes vary between 3.5% and 8.5%, most intercepts (±SD) include zero. Correlation coefficients (not included) vary between 0.988 for 4,4′-DDT, and 0.998 for malaxon, chloropyriphos and endosulfan I. LODs vary between 0.005 $\mu g\,L^{-1}$ for diazinon and endosulfan I, and 0.05 $\mu g\,L^{-1}$ for 4,4′-DDT. LOIs vary between 0.012 and 0.048 $\mu g\,L^{-1}$. In comparison between LOIs and LODs, it was found that LOIs are generally higher than LODs, but for some OCPs are slightly higher than their respective LODs, which is attributed to the more specificity of their mass spectra; making them easily searchable.

Precision and recovery results at three fortified concentrations are presented in Table 2 for both extraction methods. Recoveries vary between 84% and 102%. Uncertainties of recoveries reported as RSD% (precision) vary between 3% and 12%. Uncertainty values decrease as the fortified concentration increases, and are larger for the SPE method.

The method was evaluated by analyzing thirty surface water samples collected from various locations in Jordan. One of the samples revealed the presence of a single pesticide identified as 4,4′-DDE as shown in Fig. 3, with a concentration of 0.08 $\mu g\,L^{-1}$.

4. Discussion

To give this study a perspective, we have to stress that our major objective is to explore the merits of the full-scan MS

Table 1
Retention times, regression results[a], limits of detection (LODs)[b], identification mass ranges, limits of identification (LOIs) and guideline values (GVs) for targeted pesticides

Peak no.	Pesticide	Retention time (min)	Slope (SD)	Intercept (SD)	LOD ($\mu g\,L^{-1}$)	Mass range (u)	LOI ($\mu g\,L^{-1}$)	GV ($\mu g\,L^{-1}$)
1	α-HCH (c)	10.3	1.97(0.05)	0.04(0.06)	0.015	70–230	0.024	1[c,d]
2	β-HCH (c)	11.2	1.02(0.03)	0.04(0.05)	0.02	70–230	0.036	1[c,d]
3	Diazinon (d)	11.6	4.59(0.08)	0.13(0.08)	0.005	100–310	0.012	20[c]
4	Malaxon (c)	14.1	1.94(0.07}	0.07(0.09)	0.02	70–230	0.048	–
5	Alachlor (d)	14.3	3.08(0.06)	−0.06(0.08)	0.01	70–280	0.012	2[c], 20[d]
6	Fenitrothion (c)	15.8	1.48(0.05)	−0.02(0.04)	0.03	70–290	0.036	10[e]
7	Malathion (c)	16.4	1.97(0.04)	0.10(0.07)	0.02	90–300	0.024	100[c]
8	Chloropyriphos (d)	16.9	1.86(0.05)	0.04(0.06)	0.02	90–320	0.024	20[c]
9	Parathion (c)	17.5	2.53(0.06)	0.03(0.05)	0.02	70–300	0.024	9[c]
10	Primiphosethyl (IS)	18.3						
11	Endosulfan I (c)	20.9	4.87(0.09)	0.16(0.09)	0.005	140–350	0.012	0.22[c]
12	4,4′-DDE (d)	22.0	2.33(0.04)	0.09(0.11)	0.01	100–350	0.012	1.1[c], 2[d]
13	Endrin (c)	23.1	1.36(0.05)	0.03(0.05)	0.03	100–350	0.036	2[c]
14	Endosulfan II (c)	23.7	0.79(0.04)	−0.01(0.04)	0.05	140–350	0.048	0.22[c]
15	4,4′-DDT (d)	26.0	1.05(0.12)	−0.03(0.05)	0.02	100–330	0.024	1.1[c], 2[d]

[a] Based on three replicates of eight concentrations in the ranges: (c) 0.048–1.2 0 $\mu g\,L^{-1}$ and (d) 0.024–0.60 $\mu g\,L^{-1}$.
[b] Four replicates at: (c) 0.19 $\mu g\,L^{-1}$ and (d) 0.096 $\mu g\,L^{-1}$.
[c] U.S. Environmental Protection Agency (EPA).
[d] World Health Organization (WHO).
[e] Australia.

method in simultaneous identification and quantitation of pesticide residues in surface water. Optimization of extraction methods is a minor objective to reduce the baseline noise and we do not claim that it is a significant development in the method.

A reliable method for determination of 14 pesticide residues in surface water was reported. The method is based on LLE followed by full-scan GC–MS for separation, simultaneous identification and quantitation of targeted pesticides. Statistical results are within the ranges reported in standard methods. This method has the capabilities of identification of all separated compounds, regardless of being analytes or endogenous compounds.

The full-scan method is standard in all MS detectors and it is easy to optimize, by just selecting the time and acquisition mass range, and it is insensitive to small variations in operating conditions leading to changes in retention times and mass ions (m/z) values. Identification of eluted peaks regardless of being analytes or endogenous compounds could be performed while the run is going on.

The reliable estimation of LOIs is a unique feature of the full-scan method, since it is based on “multi ion criteria” rather than “three or four ion criteria” as in SIM and MS/MS methods. Also it is based on a numerical measure of spectral uniqueness calculated by comparison to a large and appropriate library of mass spectra rather than abundance ratios between selected ions as in SIM and MS/MS methods [13,16].

Table 2
Average recoveries and relative standard deviations (RSD, %) fortified at three concentration levels

	Pesticide	Liquid–liquid extraction ($n=4$)				Solid-phase extraction ($n=4$)			
		0.053 ($\mu g\,L^{-1}$)	0.105 ($\mu g\,L^{-1}$)	0.300 ($\mu g\,L^{-1}$)	0.600 ($\mu g\,L^{-1}$)	0.053 ($\mu g\,L^{-1}$)	0.105 ($\mu g\,L^{-1}$)	0.300 ($\mu g\,L^{-1}$)	0.600 ($\mu g\,L^{-1}$)
1	α-HCH	–	88 (7)	93 (6)	96 (4)	–	93 (12)	89 (8)	95 (7)
2	β-HCH	–	96 (10)	102 (9)	94 (7)	–	92 (11)	97 (10)	97 (6)
3	Diazinon	94 (6)	99 (5)	97 (3)	–	98 (9)	97 (6)	102 (5)	–
4	Malaxon	–	92 (8)	97 (7)	102 (3)	–	87 (10)	94 (9)	98 (5)
5	Alachlor	97 (6)	98 (3)	99 (3)	–	89 (11)	93 (9)	96 (7)	–
6	Fenitrothion	–	92 (7)7	94 (5)	97 (5)	–	96 (9)	97 (7)	98 (7)
7	Malathion	–	95 (8)	93 (7)	98 (5)	–	100 (11)	98 (9)	102 (7)
8	Chloropyriphos	98 (6)	101 (5)	99 (4)	–	96 (8)	102 (8)	98 (7)	–
9	Parathion	–	97 (6)	98 (5)	97 (4)	98 (8)	96 (7)	95 (6)	–
10	Primiphosethyl (IS)								
11	Endosulfan I	–	99 (7)	96 (5)	99 (4)	–	96 (11)	102 (9)	99 (7)
12	4,4′-DDE	89 (9)	93 (8)	96 (6)	–	96 (13)	99 (11)	98 (9)	–
13	Endrin	–	96 (8)	97 (5)	99 (5)	–	93 (12)	96 (10)	95 (8)
14	Endosulfan II	84 (9)	93 (6)	96 (5)	–	92 (11)	93 (8)	96 (7)	
15	4,4′-DDT	89 (8)	96 (7)	97 (5)	–	93 (12)	96 (8)	98 (5)	–

To evaluate the identification confidence of LODs obtained by the full-scan method, we performed a library search on full-scan GC–MS chromatograms of surface water samples spiked by LOD concentrations of targeted pesticides. Nine of them were identified among the best five selected, while the other five were among the best 10 selected. When the library search was limited to compounds containing carbon, hydrogen, nitrogen, oxygen, phosphorous and chlorine atoms, all 14 targeted pesticides were identified among the best 5 selected. Indeed, LODs obtained from the full-scan method satisfy both detection and identification of analytes.

The full-scan method is less sensitive than SIM and MS/MS methods; however, extreme sensitivities are not always required. To prove that, a comparison was made between LOIs and guideline values (GVs) for drinking water [17] as shown in Table 2. GVs are concentration limits for water contaminants set by health and environmental organizations indicating potential health problems if contaminant concentrations exceed GVs. LOIs for endosulfan I and II are 3–10 times lower than their respective GVs, while for the rest of targeted pesticides LOI values are >10 times lower than their GVs.

Sensitivity in full-scan method could be further improved by excluding acquisition of ions responsible for baseline noise and not part of identification ions in targeted analytes, such as the ion m/z 149 U in our case which came from extracted phthalate compounds available in surface water.

Recently, Gonclaves and Alpenduarda reported a GC/MS method for monitoring pesticide residues in drinking water [18]. The method is based on solid phase micro extraction (SPME) and evaluates different MS methods including the full-scan method for measurement of concentrations. They reported LODs for some of targeted pesticides included in this study. Some values are two to five times lesser than obtained in Table 1. While this is expected, since drinking water has lower matrix effects than surface water, they were setting the MS filament current at 50 μA, five times higher than in our method.

In a series of measurements, 250 mL samples were employed instead of 500 mL samples. Statistical parameters did not change significantly, but an increase of LODs and LOIs by a factor up to two was obtained for most compounds.

Acknowledgements

The authors would like to thank the National Center of Agriculture Research and Technology Transfer (NCARTT) in Jordan for supplying pesticide standards. This project was funded by the faculty of scientific research, Jordan University of Science and Technology. Project 3/2000.

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