ELSEVIER

Journal of Chromatography A, 736 (1996) 219–228

JOURNAL OF CHROMATOGRAPHY A

Analysis of organophosphorus insecticides from environmental samples using solid-phase microextraction

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Received 4 September 1995; revised 11 December 1995; accepted 12 December 1995

Abstract

Techniques for the analysis of pesticides are often complicated and time consuming. Solid-phase microextraction (SPME) using polyacrylate has been applied as an alternative simple method for the analysis of 20 organophosphorus insecticides from environmental water samples. Detection limits at the ng/l level were achieved using selective detectors such as a nitrogen–phosphorus detection (NPD) system or mass spectrometry (MS). A wide linear range was obtained with precision typically below 15% R.S.D. Contaminated soil samples were qualitatively analyzed for the presence of the target analytes. Water samples from Southern Ontario were successfully analyzed qualitatively and quantitatively.

Keywords: Environmental analysis; Water analysis; Pesticides; Organophosphorus compounds

1. Introduction

Organophosphorus insecticides (OPPs) have been used extensively for agricultural purposes for more than 40 years. There are some 200 different OPPs available in the marketplace, accounting for some 45% of the registered pesticide in the USA alone [1,2]. The utilization of this class of pesticides is favored over their more persistent organochlorine counterparts because of their ability to degrade more readily in the environment. OPPs have been found in groundwaters, surface waters, lagoons, and drinking water in varying concentrations, and therefore there is an increasing environmental concern with regard to these compounds [3,4].

Prior to the instrumental analysis of environmental samples, extensive sample extraction and pre-concentration is often required. The most difficult and time-consuming step is extraction of the target analytes from the matrix. Several methods have been developed to accomplish this often difficult task, including predominant analytical techniques such as liquid–liquid extraction (LLE) [5,6], solid-phase extraction (SPE) [4,7], or supercritical fluid extraction (SFE) [8]. The most popular technique used by environmental agencies involves some form of LLE. The procedure itself is time-consuming, tedious, and often requires pre-concentration of the extract prior to analysis. The requirement of large quantities of expensive, toxic solvents that can be harmful to the environment is one of the biggest concerns with this method. SPE has increased in popularity as an alternative for sample preparation as it overcomes a few of the disadvantages encountered with LLE. It

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0021-9673/96/$15.00
SSDI 0021-9673(95)01349-0

requires smaller amounts of solvent and is not as time-consuming. However, disadvantages include significant background interferences, as well as plugging and poor reproducibility between cartridges. SFE has become an important analytical sample preparation technique since it requires less time to achieve the extraction and uses a fraction of the solvents used by SPE and LLE. However, SFE methods require large amounts of high-purity CO_2 or other gases that can be very expensive, and are generally not very portable.

Recently a commercially available technique, solid-phase microextraction (SPME) [9–11], allows simultaneous extraction and pre-concentration of analytes from a sample matrix. In addition, it is significantly more rapid and simpler than both LLE and SPE, and the requirement of solvents has been eliminated. The SPME device consists of two major components: the syringe assembly and fiber assembly. The syringe serves as a holder for the fiber assembly which is comprised of a needle that protects a small-diameter fused-silica fiber that has been coated with a liquid polymeric stationary phase. During sampling the coated fiber is directly exposed to the sample or to the headspace above the sample, allowing absorption of the analytes according to their affinity toward the fiber coating. The analytes are thermally desorbed from the fiber in the hot injector of a gas chromatograph and are subsequently analyzed. The fiber can immediately be used for a succeeding analysis.

Investigation of different stationary phases, concentrating on polydimethylsiloxane and polyacrylate, provided evidence that a variety of different groups of analytes can selectively be extracted. SPME has been successfully applied to the analysis of both polar and non-polar analytes from solid, liquid, or gas phases. Initial investigations using this technique concentrated on volatile analytes such as BTEX (benzene, toluene, ethyl benzene, and xylene) [12,13] and volatile chlorinated hydrocarbons [14,15]. Further studies progressed into the analysis of semi-volatile groups of compounds from aqueous matrices including phenols [16,17], polycyclic aromatic hydrocarbons, and polychlorinated biphenyls [18]. The analysis of nitrogen-containing herbicides and various other pesticides has also been successfully accomplished using SPME [19,20]. This paper will focus on solid-phase microextraction of 20 phosphorus-containing insecticides from water and soil, that are currently analyzed via various EPA methods [5]. Many of these target insecticides are applied frequently to golf courses in Japan and are posing a danger of runoff to adjacent surface waters and leaching into the underlying aquifers, potentially contaminating groundwater.

2. Experimental

2.1. SPME fibers

The SPME device was purchased through Supelco Canada. The fiber assemblies purchased were coated with either 85-μm polyacrylate, or 100-μm polydimethylsiloxane (Supelco). All fibers were conditioned in the hot injection port of the gas chromatograph according to instructions provided by the supplier.

2.2. Reagents

The standard mixture (refer to Table 1) was a combination of EPA 8270 Organophosphorus Pesticide Mix (2000 mg/l in hexane–acetone, 80:20, v/v) and Organophosphorus Pesticide Mix A (2000 mg/l in hexane–acetone, 9:1, v/v) as well as isoxathion, fenitrothion, iprofenfos, EPN, and diazinon (Wako Pure Chemical ≥98–99%). A working standard containing a combination of 20 compounds (approximately 200 mg/l of each component) was prepared in methanol every week.

All aqueous solutions were prepared with NANOpure water (ultrapure water system, Barnstead). Blank analyses were carried out regularly to ensure the water was not contaminated with the target analytes.

All glassware and stir bars were cleaned with Sparkleen detergent and copious amounts of water.

2.3. Instrumentation

Preliminary experiments were done with a Varian 6000 gas chromatograph equipped with a 'split/splitless' injector and a flame ionization detection (FID) system. Separations were conducted on a PTE-5, 30 m×0.25 mm I.D., with a phase thickness of 0.25 μm (Supelco Canada), using the following

temperature program: 50°C hold for 3 min, 20°C/min to 170°C hold for 1.5 min, 10°C/min to 190°C hold for 2 min, 10°C/min to 290°C hold for 1 min. The injector was used in the splitless mode at 250°C for SPME and direct solvent injections. The carrier gas was UHP helium (1 ml/min). The FID system was maintained at 300°C, with hydrogen and air flows of 45 and 280 ml/min, respectively.

Subsequent analyses were performed with either a Varian 3400 *CX* series gas chromatograph equipped with a nitrogen–phosphorus (NPD) or a Varian Saturn ion trap mass spectrometric (IT-MS) detection system. Both instruments were equipped with a septum programmable injector (SPI). The separations were carried out under the same conditions as described above. NPD was optimized with the following flows: ECD-grade helium (1 ml/min), N_2 make (ca. 30 ml/min), air (175 ml/min), and H_2 (3.1 ml/min). The transfer line and ion-trap manifold were held at 250°C. The detector was turned off for the first 300 s of the analysis. The mass range scanned was 35 to 500 amu. The mass spectrometer was operated in the electron-ionization (EI) mode and tuned to decafluorotriphenylphosphine (DFTPP) using FC-43.

All preliminary experiments were performed using both commercially available fiber coatings, polydimethylsiloxane (100 μm) and polyacrylate (85 μm). This included desorption, and generation of time profiles. Optimum desorption conditions were determined by testing different temperatures for different times. Time profiles for each analyte in the mixtures were generated for both fiber coatings to determine the equilibration times for each of the analytes. This was achieved by exposing the fiber coating to the aqueous standards with the same concentration for exposure times between 5 and 720 min. The equilibration time for each analyte was determined by plotting the response of the gas chromatograph (GC) in area counts against the exposure time. The point at which the curve levels off within experimental error was selected as the equilibration time.

2.4. Analytical procedure

Aqueous standards were prepared by spiking an appropriate amount of the working standard into 4.6-ml clear vials (Supelco Canada) filled with 4 ml of NANOpure water, that were sealed with hole caps and Teflon-faced silicone septa (Supelco Canada). There was approximately 0.5 ml of headspace present after the addition of the water and stir bar. The needle of the device was placed in this headspace to prevent wicking of the sample, into the needle, during the direct extraction process. The fiber was immersed in the sample for 45 min under stirring at room temperature (ca. 23°C). After extraction, the fiber was directly exposed to the hot injection port of the GC for subsequent analysis. Triplicate analyses were performed for all experiments except for the study of precision where seven extractions were carried out.

2.5. Optimization

The effects on extraction efficiency from matrix interferences such as ionic strength or various pH levels of a sample were investigated. The ionic strength was modified by the addition of NaCl in varying amounts to attain a solution containing 10, 20, 30 or 40% (w/w). Aqueous standards were prepared by spiking an appropriate quantity of working standard into the salt solutions rather than water. In order to investigate the effect of pH from 2 to 11, a universal buffer, containing boric acid, citric acid, and trisodium orthophosphate, was prepared according to Perrin and Dempsey [21]. This experiment was performed by spiking appropriate quantities of standards into a buffered solution as opposed to purified water to generate standard solutions. The standards extracted under various ionic strengths and pH levels were compared with control samples (pH 7, no salt).

Precision was determined with a minimum of seven extractions from standard aqueous solutions having a concentration of 500 μg/l for FID, and 10 μg/l for MS and NPD. The percent relative standard deviation (%R.S.D.) was calculated for each of the compounds. The linearity of the method was tested by FID, NPD, and MS, by extracting aqueous standards, in duplicate, with increasing concentrations over a range typically between 0.01–1000 μg/l. The detection limits for each detector were calculated from the obtained results. In general, the detection limit is defined as the concentration of an

analyte in a sample which gives rise to a peak with a signal-to-noise ratio (S/N) of 3.

2.6. Sample analysis

Aqueous environmental samples were taken from Lake Ontario. Laboratory-prepared soil samples were prepared in the laboratory by spiking two commercially available insecticides to non-contaminated top soil. The top soil and insecticides (diazinon and chlorpyrifos) were purchased from a local hardware store (Canadian Tire). Non-contaminated top soil (500 mg) and 4 ml of water were combined in a 4.6 ml vial. The sample was stirred vigorously, allowing the soil and water to mix. The fiber was exposed directly to the sample. GC–IT-MS was used to confirm that the soil was not contaminated with target analytes. The insecticides were prepared in water according to the manufacturer's instructions. An aliquot (100 ml) of this solution was added to 35 g of top soil, mixed and left overnight in a sealed container. An aliquot (4 ml) of the water layer was analyzed using SPME–GC–NPD and SPME–GC–MS.

3. Results and discussion

SPME is an equilibrium process that involves the partitioning of analytes from a liquid or gaseous sample into the polymeric phase according to their partition coefficients, K [10]. The following equation may be used to describe the SPME process of a two-phase system:

$$n_s = \frac{KV_sV_{aq}C^0_{aq}}{KV_s + V_{aq}} \quad (1)$$

where n_s is the amount extracted by the fiber coating, V_{aq} and V_s are the volumes of the aqueous phase and stationary phase, respectively, and C^0_{aq} is the initial concentration of the analytes in the aqueous phase. Eq. 1 indicates that the amount of analytes extracted is dependent on both the volume of the stationary phase and the partition coefficient. There is a linear relationship between the amounts extracted and the initial concentrations of the analytes in the aqueous phase; therefore, the sensitivity and the linear range of the method are also dependent upon these parameters. Hence, the selection of an appropriate stationary phase is extremely important.

Fig. 1 illustrates a comparison of the amounts extracted using polydimethylsiloxane (PDMS) and polyacrylate (PA) coated fibers from a 50 μg/l standard solution. For this comparison the maximum amount available for the extraction of methyl parathion and disulfoton was 400 ng while for the remaining 18 compounds it was 200 ng. Since the organophosphates in general are considered polar, it is expected that the analytes have a higher affinity for the polyacrylate coating. Although the polydimethlysiloxane coating can extract the target analytes, it does so to a lesser extent. The affinity that different analytes have towards the two phases is also illustrated by their partition coefficients, K. The K value for each analyte was calculated based on extractions performed under equilibrium conditions (120 min). These results are listed in Table 1.

Since SPME is a process dependent on equilibrium rather than total extraction, the amount of analyte extracted at a given time is dependent on the mass transfer of an analyte through the aqueous phase [22]. All experiments were performed under agitation in order to optimize the transfer of analytes from the aqueous sample into the fiber coating. The length of time required to reach equilibrium also decreases under these conditions. All of the analytes excluding isoxathion reached equilibrium conditions by 45 min for the polyacrylate coating (refer to Table 1). Although isoxathion does not reach equilibrium by 45 min, the amount extracted at this time is still greater than 50% of the amount extracted at 75 min, when equilibrium has been attained. Therefore the extraction time selected for the method is 45 min, since the majority of analytes then has reached equilibrium.

Optimum desorption conditions were determined by testing various temperatures for different lengths of time. The time chosen for desorption was 3 min in an injector port set to 250°C. Under these conditions, an optimal amount of analyte was transferred with minimal carryover occurring in a subsequent analysis (fiber blank). All further method development and validation was completed with the polyacrylate coating since optimal extraction amounts and times were achieved with this fiber coating. Fig. 2 illus-

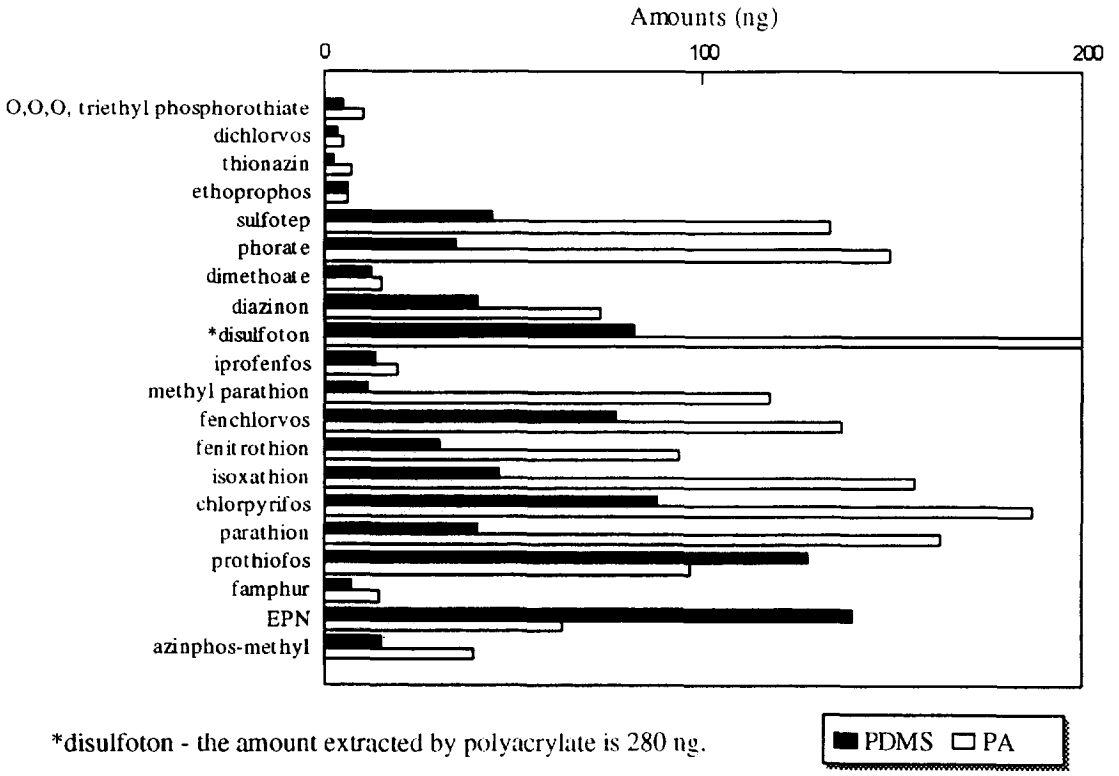

Fig. 1. Comparison between the extraction efficiency of a 85-μm polyacrylate (PA) and 100-μm polydimethylsiloxane (PDMS) coated fiber

trates the successful extraction and separation of a 1 μg/l solution using a polyacrylate coating, analyzed by GC–NPD.

The addition of salt, such as NaCl, to a sample would decrease the solubility of the analytes in the aqueous phase which favors movement of the analytes into the fiber coating, thereby improving the extraction efficiency of the method. In general, as Fig. 3 illustrates, increasing the ionic strength causes a decrease in the amounts extracted. This is true for the target analytes in the phosphorothiate group (Fig. 3a). The exception to this trend is for O,O,O-triethylphosphorothiate and thionazin, which are slightly less polar and therefore would be expected to show an increase in the amount extracted with the addition of increasing amounts of salt, as was noted. The extracted amounts of the first four analytes in Fig. 3b increase or decrease with the addition of salt depending on the solubility and polarity of the compounds. For example, extraction of ethoprophos increases with increasing ionic strength, suggesting that its solubility in water is decreased. The remaining six compounds in Fig. 3b are phosphorodithioates and all decrease in amount extracted with increasing amount of salt. Varying the pH over a range from 2 to 11 did not significantly affect the extraction of the analytes by the fiber, therefore no further comparisons with pH adjustments were performed. The effects of pH and ionic strength can be incorporated into a method that focuses on a specific analyte or group of analytes in order to improve and enhance the extraction efficiency of the method. Since this study targeted a broad range of analytes, it is not surprising that optimum conditions for one group may be detrimental to another group. Therefore, method optimization was performed under neutral conditions (no salt, or pH adjustments).

The linearity of the method was tested by FID, NPD, and MS by extracting aqueous standards, with increasing concentrations, over a range typically from 5 to 1000 μg/l with GC–FID and 0.01 to 500 μg/l, using GC–NPD or GC–MS. Regression analy-

Table 1
Physical properties of the target pesticides under investigation

Target analyte	Formula[a]	M_r	Solubility in water[a] (mg/l)	Equilibrium time		K values	
				PDMS	PA	PDMS	PA
Azinphos-methyl	$C_{10}H_{12}N_3O_3PS_2$	317.1	33	30	15	350	2400
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	350.6	2	90	45	4500	150 000
Diazinon	$C_{12}H_{21}N_2O_3PS$	304.36	40	60	40	1500	6000
Dichlorvos (DDVP)	$C_4H_7Cl_2O_4P$	220.98	10 000	30	30	130	300
Dimethoate	$C_5H_{12}NO_3PS_2$	229.2	25 000	30	25	350	800
Disulfoton	$C_8H_{19}O_2PS_3$	274.4	25	60	45	1600	22 000
EPN	$C_{14}H_{14}NO_4PS$	323.3	n.a.	90	25	4000	4100
Ethoprophos	$C_8H_{19}O_2PS_2$	242.3	750	15	40	180	300
Ethyl parathion	$C_{10}H_{14}NO_5PS$	291.3	24	60	45	1100	45 000
Famphur	$C_{10}H_{16}NO_5PS_2$	325.3	sparingly	60	30	150	700
Fenchlorvos	$C_8H_8Cl_3O_3PS$	321.57	40	120	45	3500	22 000
Fenitrothion	$C_9H_{12}NO_5PS$	277.2	14	60	30	1000	9100
Iprofenfos (IBP)	$C_{13}H_{21}O_3PS$	288.4	1000	30	40	400	1000
Isoxathion	$C_{13}H_{16}NO_4PS$	313.3	1.9	90	75	1800	37 400
Methyl parathion	$C_8H_{10}NO_5PS$	263.2	55	30	40	130	4000
O,O,O-Triethyl phosphorothiate	$C_6H_{15}O_3PS$	198.03	n.a.	30	40	180	500
Phorate	$C_7H_{20}O_2PS_3$	260.4	50	90	40	1200	27 000
Prothiofos	$C_{11}H_{15}Cl_2O_2PS_2$	345.2	1.7 mg/kg	60	45	10 000	9800
Sulfotep	$C_8H_{20}O_5P_2S_2$	322.3	25	90	40	1600	20 000
Thionazin	$C_8H_{15}N_2O_3PS$	248.2	1140	15	40	50	400

n.a.: not available.
[a]Information taken from Refs. [5,23,24].

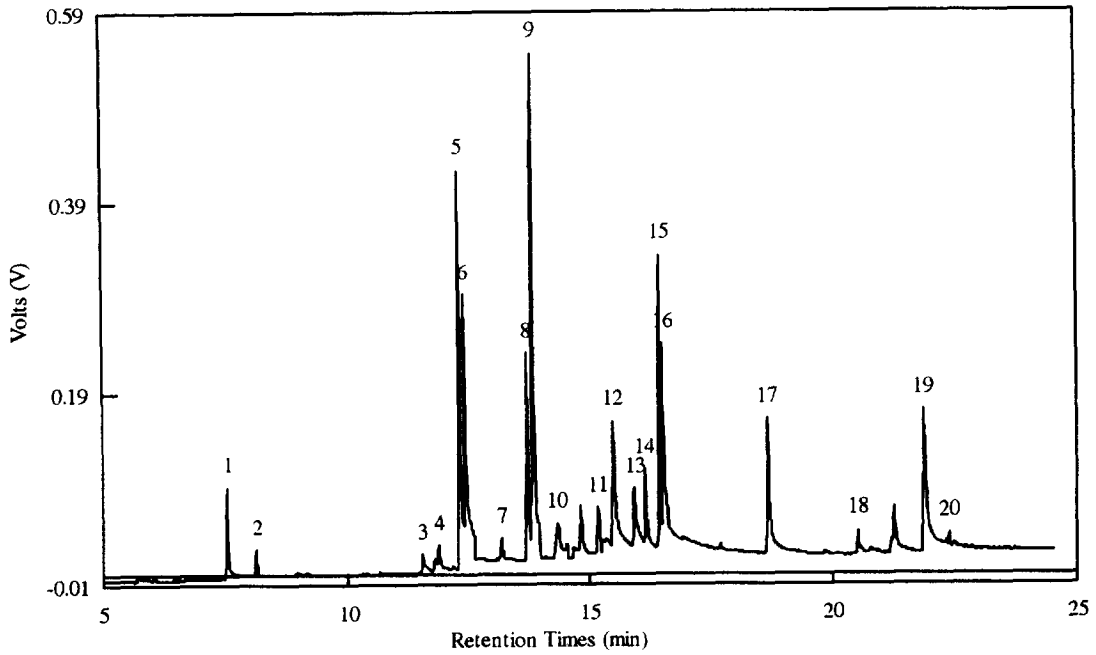

Fig. 2. Analysis of a 1 μg/l aqueous standard by SPME–GC–NPD. Peaks: 1, O,O,O triethylphosphorothiate; 2, dichlorvos; 3, thionazin; 4, ethoprophos; 5, sulfotep; 6, phorate; 7, dimethoate; 8, diazinon; 9, disulfoton; 10, iprofenfos; 11, methyl parathion; 12, fenchlorvos; 13, fenitrothion; 14, isoxathion; 15, chlorpyrifos; 16, ethyl parathion; 17, prothiofos; 18, famphur; 19, EPN; 20, azinphos-methyl.

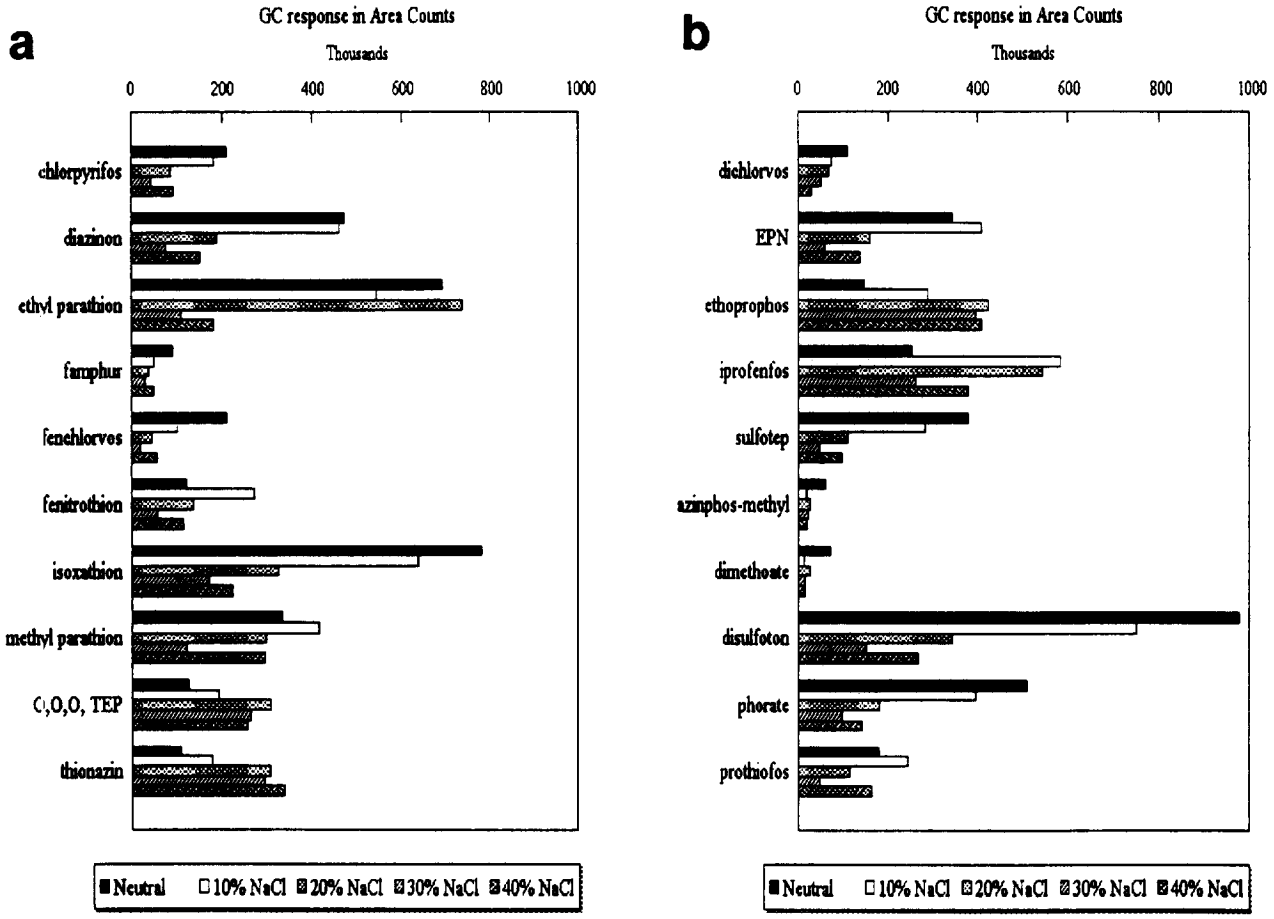

Fig. 3. Effects of different salt concentrations on the extraction efficiency.

sis was used to approximate the linearity of the calibration curves generated by the detector. All of the analytes analyzed were found to be linear over a minimum of two orders of magnitude and had correlation coefficients, r^2, from 0.98 to 1.00. The linear range of the SPME method coupled with either GC–NPD or GC–MS was extended to include one more order of magnitude.

The linear-range experiments provided the necessary information to estimate the limits of detection (LODs), based on the lowest detectable peak that had $S/N=3$. The detection limits estimated for SPME coupled with the three detectors is listed in Table 2. A typical noise reading encountered when operating FID fell in a range of 750–1000 area counts. Therefore, based on a noise level of 1000 area counts and an S/N of 3, an area count of 3000 was considered to be an appropriate estimate for the smallest detectable peak. The detection limits estimated using the Varian GC–FID system were much higher than those obtained using EPA methods. This is due to the poor detection of the organophosphorus pesticides by FID. The same estimation was made for the experiments performed with NPD. However, it was noticed that the noise on the NPD system was much smaller, allowing for an even lower area count (1500) to be used for the lowest detectable peak. As a result, lower LODs were determined for NPD, which is expected since this detector is more selective and sensitive towards phosphorous-, nitrogen-, and sulfur-containing compounds. Many of the estimated LODs for the target analytes using GD–NPD

Table 2
Estimated detection limits of standard US EPA methods compared to detection limits and precision for FID, ECD, and MS coupled with SPME

Target analyte	FID (ng/l) (%RSD; $n = 7$)	NPD (ng/l) (%RSD; $n = 7$)	MS (ng/l) (%RSD; $n = 7$)	Quantitation ion	Standard EPA method (ng/l)
Azinphos-methyl	5000 (18)	280 (6)	3 (8)	160	9[a] 1500[c]
Chlorpyrifos	780 (14)	17 (11)	2 (12)	314	4a
Diazinon	900 (13)	26 (8)	2 (14)	305	38[a] 200[b] 600[c]
Dichlorvos (DDVP)	1350 (13)	500 (5)	6 (6)	109	100[c] 2500[a]
Dimethoate	5200 (21)	50 (9)	73 (2)	230	27[a]
Disulfoton	900 (14)	12 (9)	3 (9)	89	32[a] 300[b]
EPN	250 (19)	15 (10)	8 (15)	157	9[a] 300[c]
Ethoprophos	280 (13)	161 (8)	100 (8)	243	n.a.
Ethyl parathion	1960 (16)	9 (14)	5 (15)	292	18[a] 300[c]
Famphur	1400 (19)	310 (9)	3 (15)	218	27[a] 19000[c]
Fenchlorvos	940 (18)	15 (10)	2 (9)	285	n.a.
Fenitrothion	240 (15)	32 (9)	4 (14)	260	2000[c]
Iprofenfos (IBP)	1780 (24)	130 (6)	2 (4)	91	n.a.
Isoxathion	460 (14)	40 (6)	2 (11)	100	n.a.
Methyl parathion	1030 (16)	114 (12)	11 (14)	109	10[a]
O,O,O-Triethyl phosphorothiate	4900 (17)	260 (12)	9 (12)	198	n.a.
Phorate	690 (9)	11 (9)	2 (9)	75	10[a]
Prothiofos	540 (26)	23 (10)	2 (8)	309	n.a.
Sulfotep	470 (13)	16 (11)	2 (12)	323	6[a]
Thionazin	430 (17)	180 (7)	2 (12)	243	1000[c]

n.a.: information not available.
[a]EPA method 1657.
[b]EPA method 507.
[c]EPA method 622 or 622.1.

were comparable to those obtained by EPA methods. Finally, for the experiments coupling SPME–GC–MS the signal to noise ratios were determined by using the area of the quantification peak to the noise. At lower concentrations the *S/N*, and thus the detection limit, can be improved by analyzing more than one characteristic fragmentation ion. Referring to Table 2, it can be seen that the estimated LODs compare favorably and for some analytes are better than those achieved using standard EPA methods.

The method precision was determined under neutral conditions, by performing a minimum of seven extractions from an aqueous solution with a concentration of 500 and 10 μg/l using FID, MS, and NPD, respectively. The precision was found to be typically below 15% when using selective detectors such as NPD or MS. These results have also been included in Table 2. It is expected that the precision will improve to a greater extent if an autosampler with stirring is used for the experiments. Since the US EPA requires that a method has under 30% R.S.D., the precision of the SPME method was deemed acceptable.

The developed SPME method was then successfully applied to qualitatively and quantitatively analyze field samples. A water sample from Lake Ontario was analyzed for the presence of any of the target analytes by SPME–GC–NPD, and confirmed by SPME–GC–MS. None of the target analytes were detected in the water sample. Therefore, a mixture containing three of the target analytes, fenitrothion, isoxathion, and diazinon, in known concentrations was spiked into the lake samples and the analysis repeated. The spiked lake samples were analyzed by SPME–GC–MS (Fig. 4) and the amounts extracted quantitatively determined (refer to Table 3) using external calibration. The percent recovery was calculated by dividing the amounts extracted by the fiber coating by the initial amounts that were spiked into the sample and then multiplying by 100. Taking into consideration the %R.S.D. reported for each compound and slight matrix interferences that may be present in the sample, approximately 100% recovery was attained for the three target analytes.

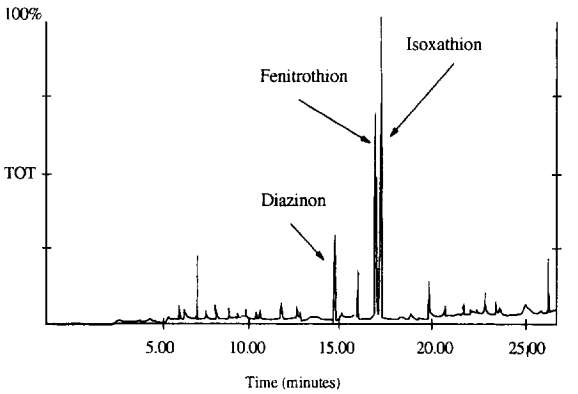

Fig. 4. Extraction of a Lake Ontario sample using SPME–GC–MS spiked with fenitrothion, isoxathion, and chlorpyrifos.

Contaminated soil samples containing the target analytes under investigation were not available, therefore soil samples were prepared in the laboratory. The top soil purchased from the local hardware store was analyzed by SPME–GC–MS and it was found that none of the target analytes were present. This soil analysis was then used as a blank for laboratory-prepared contaminated soils. The water layer above the soil sample was directly analyzed by SPME–GC–NPD, producing two peaks that were positively identified to be diazinon and chlorpyrifos by SPME–GC–MS. The results indicated that direct extraction of either a slurry in the blank sample or from the slurry was possible and that the soil did not significantly interfere with the extraction.

Table 3
Quantitative results for a lake-sample spiked with fenitrothion (MEP), isoxathion, and diazinon

Target analytes	Lake sample not spiked (ng)	Amount spiked into sample (ng)	Amount detected in spiked lake sample (ng) (%R.S.D.)	% Recovery
Diazinon	0	142	136 (6.46)	96
Fenitrothion	0	565	566 (0.56)	100
Isoxathion	0	294	301 (2.25)	102

All of the target analytes under investigation were not found in the lake sample and were therefore excluded from the table.

4. Conclusions

This paper has detailed the method development and validation of an SPME procedure that can be applied to the analysis of organophosphorus insecticides from environmental samples. The method is precise and can be used over a wide linear range. Detection limits at the part per trillion level were achieved when using SPME–GC–MS. These limits are comparable to those reported by the US EPA using conventional methods. Qualitatively, the method can be applied as a screening device to detect the presence of organophosphorus insecticides in soil. It can also be applied to the analysis of aqueous environmental samples for both qualitative and quantitative determinations. The compact nature of the device and the simplicity of the procedure allows this method to be easily automated with a few modifications to a standard Varian autosampler. There is also a potential for on-site applications.

Acknowledgments

The research presented here is a continuation of the work presented at the 1994 Riva Conference, by K.J. and J.B.P. The authors wish to gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada, Varian, Supelco, and the Waterloo Centre for Groundwater Research.

References

[1] D.J. Echobichan and R.M. Joy, CRC Pesticides and Neurological Diseases, CRC Press, Boca Raton, FL, 2nd ed., 1994, p. 381.
[2] G.W. Ware, Pesticides Theory and Application, Freeman, Los Angeles, CA, 1983, p. 308.
[3] M.R. Driss, M.C. Hennion and M.L. Bouquerra, J. Chromatogr., 639 (1993) 352.
[4] W.E. Johnson, N.J. Fendinger and J.R. Plimmer, Anal. Chem., 63 (1991) 1510.
[5] T.E. Fielding and W.A. Telliard, United States Environmental Protection Agency, Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, Washington, 1992.
[6] D. Barceló, J. Chromatogr., 643 (1993) 117.
[7] L. Liska, J. Krupcik and P.A. Laclercq, J. High Resolut. Chromatogr., 12 (1989) 577.
[8] I.J. Barnabas, J.R. Dean and S.P. Owen, Analyst, 119 (1994) 2381.
[9] J. Pawliszyn, Trends Anal. Chem., 14 (1995) 113.
[10] Z. Zhang, M.J. Yang and J. Pawliszyn, Anal. Chem., 66 (1994) 844A.
[11] A.A. Boyd-Boland, M. Chai, Y.Z. Luo, Z. Zhang, M.J. Yang, J. Pawliszyn and T. Górecki, Environ. Sci. Technol., 28, No. 13, (1994) 569A.
[12] D.W. Potter and J. Pawliszyn, J. Chromatogr., 625 (1992) 247.
[13] C.L. Arthur, L.M. Killam, S. Motlagh, M. Lim, D.W. Potter and J. Pawliszyn, Environ. Sci. Technol., 26 (1992) 979.
[14] C.L. Arthur and J. Pawliszyn, Anal. Chem., 62 (1990) 2145.
[15] M. Chai, C.L. Arthur, J. Pawliszyn, R.P. Belardi and K.F. Pratt, Analyst, 118 (1993) 501.
[16] K.D. Buchholz and J. Pawliszyn, Environ. Sci. Technol., 27 (1993) 2844.
[17] K.D. Buchholz and J. Pawliszyn, Anal. Chem., 66 (1994) 160.
[18] D.W. Potter and J. Pawliszyn, Environ. Sci. Technol., 28 (1994) 298.
[19] A.A. Boyd-Boland and J. Pawliszyn, J. Chromatogr. A, 704 (1995) 163.
[20] R. Eisert and Levsen, Fresenius' J. Anal. Chem., 351 (1995) 555.
[21] D.D. Perrin and B. Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall, London, 1974.
[22] D. Lough, S. Motlagh and J. Pawliszyn, Anal. Chem., 64 (1992) 1187.
[23] C.R. Worthing (Editor), The Pesticide Manual – A World Compendium, The British Crop Protection Council, The Lavenham Press, London, 7th ed., 1983.
[24] S. Budavari, The Merck Index, Merck and Co., Rahway, NJ, 11th ed., 1989.