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Analysis of organochlorine pesticides using solid-phase microextraction

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Abstract

A solid-phase microextraction (SPME) procedure has been developed to successfully extract eighteen chlorine-containing pesticides from water. A fused-silica fiber coated with a non-polar polydimethylsiloxane stationary phase was used to extract the analytes from water samples over a concentration range of 0.001 to 100 ng/ml. Limits of detection at a ng/l level were achieved with GC and flame ionization detection, and improved to sub ng/l levels using GC–MS, or GC with electron-capture detection (ECD). The reproducibility of the measurements between fibers was found to be very good, with precision typically below 20% R.S.D. within a single fiber. Qualitative analysis was performed on river and lake samples from Southern Ontario. Samples from the Arctic region of Canada were analyzed quantitatively using a dual ECD system.

Keywords: Solid-phase microextraction; Organochlorine compounds; Pesticides; Hexachlorocyclohexanes; Diphenyl aliphatics; Cyclodienes

1. Introduction

Semi-volatile persistent organic pollutants have been detected in natural waters from a variety of different regions posing a threat on human health and the environment. These semi-volatile insecticides included DDT (dichlorodiphenyltrichloroethane), heptachlor, aldrin, dieldrin, and the hexachlorocyclohexanes, (benzene hexachlorides; BHC). Organochlorines characteristically have very low solubilities in water, are fat soluble, and are resistant to metabolism. The combination of their persistence in the environment, toxicity, and ability to bioaccumulate has caused them to be labeled as environmental hazards [1] and, consequently, many have been withdrawn from registered use [2]. This paper will focus on the analysis of chlorinated pesticides in water, that are currently investigated by EPA (Environmental Protection Agency) methods 508, 608, and 625 [3–5].

The primary step in water analysis involves the separation of the target analytes from the aqueous matrix. Several methods have been developed to accomplish this often difficult task, including the two most popular analytical techniques, liquid–liquid extraction (LLE) [3–5] and solid-phase extraction (SPE) [6,7]. The most popular technique used is LLE, which requires large quantities of expensive, toxic solvents that

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can be harmful to the environment. The procedure itself is time-consuming, tedious, and often requires pre-concentration of the sample prior to analysis. SPE has increased in popularity as a sample preparation technique because it overcomes a few of the disadvantages encountered with LLE, as it is not as time-consuming, and requires less solvent. However, disadvantages include plugging of cartridges, significant background interferences, and poor reproducibility.

Solid-phase microextraction (SPME) is a solvent-free analytical technique that is significantly more rapid and simple than the conventional methods previously mentioned [8–10]. The SPME device is commercially available and 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 into different stationary phases, concentrating on polydimethylsiloxane and polyacrylate, provides 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) [11,12] and volatile chlorinated hydrocarbons [13,14]. Further studies progressed into the analysis of semivolatile groups of compounds from aqueous matrices including phenols [15,16], polycyclic aromatic hydrocarbons, and polychlorinated biphenyls [17]. The analysis of nitrogen-containing pesticides has also been successfully accomplished using SPME [18]. This paper details the development and application of an SPME method to a different class of pesticides, the organochlorines.

2. Experimental

The SPME device consists of a reusable syringe assembly, and replaceable fiber assembly (Supelco Canada). The fiber selected for the analysis of the organochlorines was a fused-silica rod 1 cm long, coated with 100 μm of polydimethylsiloxane (PDMS). The PDMS fibers were conditioned in the hot injection port of the gas chromatograph for 2 h at 275°C. The stock standard mixture, containing 18 chlorinated compounds (2000 μg/ml in toluene–hexane 50:50, Supelco) was purchased in 1-ml aliquots. The organochlorines included in this mix are listed in Table 1. A working standard (200 μg/ml, in methanol) was prepared every two weeks.

Aqueous standards were prepared by spiking an appropriate amount of the working standard into 40-ml amber vials (Supelco, 2-3203 cleaned according to EPA 40CFR 136), filled with 35 ml of water (NANOpure, ultrapure water system, Barnstead, UK), that were sealed with hole caps and Teflon-faced silicone septa (both purchased from Supelco). All vials were silanized prior to use, by the following procedure: the glassware was washed with Sparkleen detergent and water, followed by placing them in hot H_2SO_4 for approximately 2 h. The glassware was rinsed with water and left to dry in the oven. The vials were then exposed to a 10% solution of dichlorodimethylsilane (Supelco) in toluene for at least 6 h. Finally, the vials were rinsed with toluene and methanol, dried in an oven, and stored in a dark place until use. All other glassware and cross stir bars were cleaned with Sparkleen detergent and copious amounts of water.

Preliminary investigations were performed using a Varian 6000 gas chromatograph equipped with a flame ionization detector (FID), and a split/splitless injector. Separations were conducted using a PTE-5, 30 m × 0.25 mm I.D., with a phase thickness of 0.25 μm (Supelco). The temperature program used was as follows: 45°C

Table 1
Physical properties for target organochlorine pesticides

Pesticide	Empirical formula[a]	Molecular mass[a]	Solubility in water[a]	Equilibration time[b] (mg/l)	K values[b] (min)
Hexachlorocyclohexanes					
α-BHC	$C_6H_6Cl_6$	290.8	1.63	15	1 800
β-BHC	$C_6H_6Cl_6$	290.8	0.7	15	900
δ-BHC	$C_6H_6Cl_6$	290.8	PIS	15	600
Lindane (γ-isomer)	$C_6H_6Cl_6$	290.8	7.3–10	15	13 000
Diphenyl aliphatics					
Methoxychlor	$C_{14}H_9Cl_5$	353.25	0.1	180	18 000
p,p'-DDD	$C_{14}H_{10}Cl_4$	320.1	n/a	180	21 000
p,p'-DDE	$C_{14}H_8Cl_4$	318.1	n/a	90	10 000
p,p'-DDT	$C_{14}H_9Cl_5$	345.5	0.001–0.004	180	23 000
Cyclodienes					
Aldrin	$C_{12}H_8Cl_6$	364.93	0.01–0.02	180	10 000
Dieldrin	$C_{12}H_8Cl_6O$	380.9	0.1–0.25	120	25 000
Endosulfan I	$C_9H_6Cl_6O_3S$	406.9	0.32	45	25 000
Endosulfan II	$C_9H_6Cl_6O_3S$	406.9	0.33	45	10 000
Endosulfan sulfate	$C_9H_6Cl_6O_4S$	422.9	n/a	45	400
Endrin	$C_{12}H_8Cl_6O$	380.9	0.23	120	21 000
Endrin aldehyde	$C_{11}H_6Cl_6O$	368.9	n/a	120	1 400
Endrin ketone	$C_{12}H_8Cl_6O$	380.9	n/a	45	2 300
Heptachlor	$C_{10}H_5Cl_7$	373.3	0.056	180	18 000
Heptachlor epoxide	$C_{10}H_5Cl_7O$	389.3	0.35	180	35 000

[a] Values taken from Refs. [2,22,23].
[b] Equilibration times and K values were calculated using a 100-μm polydimethylsiloxane-coated fiber, using neutral conditions. PIS = practically insoluble in water; n/a = information is not available.

hold for 2 min, 30°C/min to 180°C hold for 1 min, 4°C/min to 229°C hold for 1 min, 3°C/min to 245°C, 10°C/min to 260°C hold for 2 min. The injector was used in the "splitless" mode and held isothermally at 275°C for SPME and direct solvent injections for the duration of the run. The carrier gas was UHP helium, at a rate of 1 ml/min through the column. The FID was maintained at 300°C, with hydrogen and air flows of 45 ml/min and 280 ml/min, respectively.

Subsequent analyses were performed with either a Varian 3400 gas chromatograph, equipped with an electron-capture detector (ECD), or a Varian Saturn ion-trap mass spectrometric detector (MS). Both the GC–ECD and GC–MS were equipped with septum programmable injectors (SPI). The same column and temperature program described above were used for the separations. The transfer line and ion-trap manifold were held at 275°C. In order to prevent overloading of the electron multiplier by the solvent peak, the detector was turned off for the first 300 s of the analysis. The mass range scanned was 35 to 450 a.m.u. as specified in U.S. EPA method 625 [3]. The mass spectrometer was operated in the electron ionization (EI) mode and tuned to decafluorotriphenylphosphine (DFTPP).

To confirm the results obtained for the environmental samples a HP 5890 Series II gas chromatograph equipped with a conventional split/splitless injector system, and dual ECD detectors was used. The injector was used in the splitless mode and held isothermally at 275°C for SPME and direct solvent injections for the duration of the run. The carrier gas was H_2, which

was pressure-programmed to maintain a flow-rate of 1 ml/min through the column for the length of the run. Both ECDs were maintained at 325°C. The primary column used was a DB-5, 30 m × 0.25 mm I.D. with a phase thickness of 0.25 μm (J&W Scientific), and the confirmation column was a HP 50 + (50% phenyl) column, 30 m × 0.25 mm I.D., phase thickness of 0.25 μm (Hewlett-Packard Canada). The gas chromatograph oven temperature program used was as follows: 45°C hold for 5 min, 10°C/min to 150°C, 2°C/min to 250°C, and 10°C/min to 280°C. The total run time of the program is 68.50 min.

To achieve acidic conditions (pH 2–6) a buffer was prepared using glacial acetic acid and sodium acetate according to Perrin and Dempsey [19]. The alkaline solutions (pH 8–11) were prepared by adding 0.01 *M* NaOH dropwise until the desired pH was obtained. Ionic strength was adjusted with NaCl to achieve solutions containing 10% (w/w), 20% (w/w), 30% (w/w), and 40% (w/w). All these experiments were performed in triplicate, and the results were compared to control samples (pH 7, no salt) that were also analyzed in triplicate.

A minimum of seven extractions, were performed from standard aqueous solutions having a concentration of 10 ng/ml for FID and MS, and 1 ng/ml for ECD to determine precision of the method. The reproducibility of the method between fibers was also investigated by performing a minimum of eight extractions with each of three fibers on one day and comparing amounts extracted. A Varian 8200 autosampler modified to accommodate a SPME device was used to perform extractions from 14-ml silanized sample vials. A specially designed stirring mechanism was used, to ensure consistent movement of the sample. The SPME2 and Star System Version 4.0 developed by Varian were used to run the autosampler and analyze the data, respectively.

The linearity of the method was tested by FID, ECD, and MS, by extracting aqueous standards, in duplicate, with increasing concentrations over a range typically between 0.001 and 100 ng/ml. The detection and quantitation limits for each detector were calculated from the results obtained. 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.

Environmental samples for quantitative analysis were obtained through the Waterloo Centre for Groundwater Research. The aqueous samples come from the Arctic regions of Canada and Russia in the form of melted snow and glacial ice. The samples were initially screened for the presence of pollutants, by extracting overnight. Each of the three replicate samples that tested positive for the presence of chlorinated species was then analyzed in duplicate. The fiber was exposed to a 35-ml sample for 90 min and subsequently analyzed by the GC–dual-ECD method. Quantitation of the samples was performed using external calibration. River and lake samples were taken from the region of Southern Ontario and analyzed qualitatively using this SPME–GC–ECD.

3. Results and discussion

The organochlorines under investigation fall into a non-polar class with relatively high octanol–water coefficients ($\log P_{ow}$) [20], and very low solubility in water. Hence, these analytes would be expected to partition more readily into a more non-polar fiber coating rather than a polar one. To date the commercially available fibers are coated with either polydimethylsiloxane or polyacrylate. The polydimethylsiloxane polymeric coating was selected for the extraction of these analytes from the aqueous medium. The more polar polyacrylate fiber coating was also found to be successful in extracting this class of compounds; however, with lower efficiency than the PDMS-coated fiber.

Solid-phase microextraction 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 [9]. The analytes under investigation have relatively large K values; therefore under equilibrium conditions the initial analyte concentration in the aqueous phase is significantly depleted [21]. Under these conditions the SPME

process can be described by the following formula:

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

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. Likewise the sensitivity and the linear range of the method are also dependent upon these parameters. Therefore the selection of an appropriate stationary phase is extremely important.

Since SPME is a process dependent on equilibrium rather than total extraction, the amount of analyte extracted at a given time is dependent upon the mass transfer of an analyte through the aqueous phase [21]. Taking this into consideration, a shorter equilibration time can be attained by simply agitating the solution. Thus, all experiments were performed under stirred conditions.

The initial step in the development of the method involved optimizing desorption times and temperatures, followed by generating time profiles for each of the analytes. Optimization of the extraction conditions by matrix modification was investigated as a means of enhancing the amount extracted by the fiber coating. This was followed by determining the precision, and the range over which the method was linear. The limit of detection and quantitation were established from the linearity experiments. Finally, the method was applied to the analysis of real samples.

Optimum desorption conditions were determined by testing various temperatures for different lengths of time. The time and temperature required to successfully desorb all the analytes from the fiber coating with minimal carryover in a subsequent analysis (fiber blank) were considered to be the optimized desorption conditions. The condition chosen was desorption for 2 min at 275°C. Time profiles for each analyte in the mixtures were generated by extracting aqueous standards with the same concentration for exposure times between 5 and 720 min. The equilibration time for a specific analyte can be determined by plotting the area counts obtained for each analyte against the exposure time. Equilibration times ranged from 15 min to 180 min (refer to Table 1). Therefore it takes a total of 3 h for all the analytes to reach equilibrium. This is a rather lengthy extraction time; therefore the time selected to perform the sample analysis was 90 min. After 90 min the amount extracted, under stirred conditions, was still greater than half the amount extracted after equilibrium had been reached, for the majority of the analytes being studied. Choosing an extraction time that is less than the equilibration time may affect the sensitivity and precision of the method. Although equilibrium has not been reached, it is not likely that the overall sensitivity of the method will be significantly affected for these compounds since the majority have high K values (>1000). The compounds that do have slightly smaller K values have already reached equilibrium by the 90-min extraction time. The precision of the method, on the other hand, may be significantly affected when the extraction time is less than the equilibration time. Since equilibrium may not be established, slight deviations in the extraction time may result in deviations of amounts extracted. Therefore, it is essential that the extraction time be monitored carefully and that it remain within ± 2 min of the 90-min extraction time selected. The extraction of a 1 μg/l aqueous standard is illustrated in Fig. 1.

The amounts of each analyte extracted were determined under equilibrium conditions in order to calculate relative K values from Eq. 1 (refer to Table 1). The lower the K value the more soluble the analyte is in the water, and thus the lower the affinity of that analyte toward the fiber coating. Therefore, the amount of analyte extracted by the fiber can be increased if the solubility of the analyte in water is decreased. This can be achieved by altering the ionic strength by the addition of salt to the matrix or by adjusting the pH of the water. The target class of analytes for these modifications were primarily

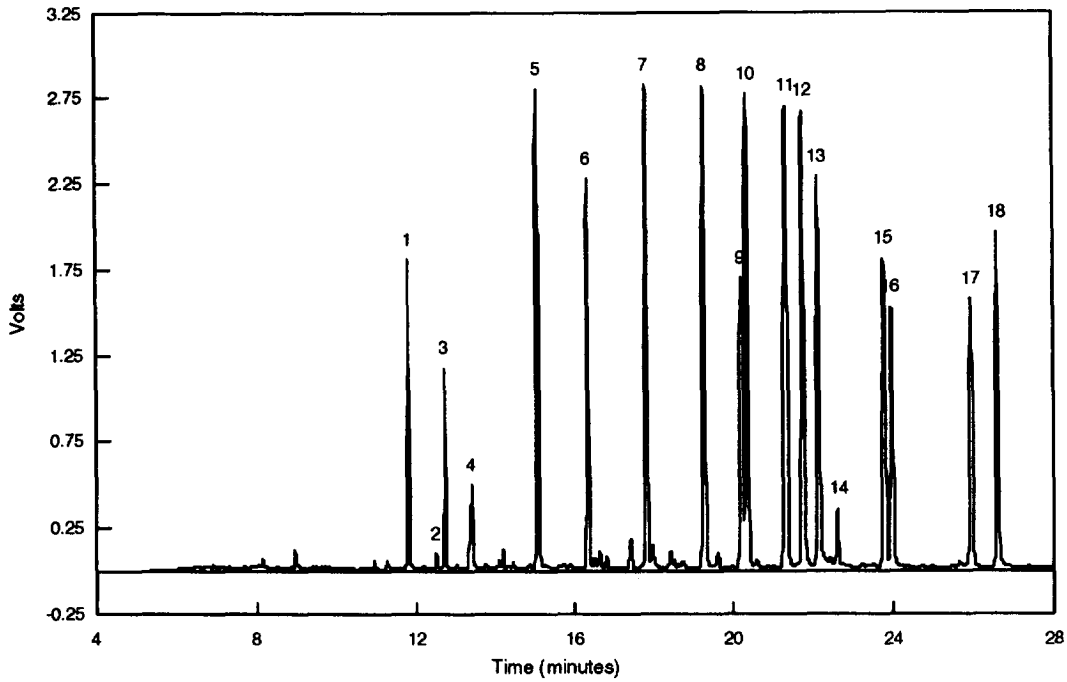

Fig. 1. Analysis of a 1 ng/ml aqueous standard using SPME–ECD. Peaks: 1 = α-BHC, 2 = β-BHC, 3 = γ-BHC (Lindane), 4 = δ-BHC, 5 = heptachlor, 6 = aldrin, 7 = heptachlor epoxide, 8 = endosulfan I, 9 = dieldrin, 10 = p,p'-DDE, 11 = endrin, 12 = endosulfan II, 13 = p,p'-DDD, 14 = endrin aldehyde, 15 = endosulfan sulfate, 16 = p,p'-DDT, 17 = endrin ketone, 18 = methoxychlor.

the BHC compounds, and other analytes with a K value less than 10 000. The effect of ionic strength on the extraction efficiency was determined by analyzing solutions containing different amounts of NaCl (Fig. 2). Generally, it was observed that 10% and 20% (w/w) NaCl increased the amount extracted by the fiber. Overall the addition of 10% (w/w) NaCl was the most successful as it increased the amounts extracted for twelve out of the eighteen compounds. The focus of this experiment was placed on those analytes that were poorly extracted under neutral conditions, and 20% (w/w) NaCl was determined to be the optimal salt condition for extraction of these analytes. The addition of higher concentrations of salt to the sample either provided results that were similar to the previous two concentrations discussed, or caused a decrease in the amount extracted in comparison to the neutral conditions. Varying the pH over a range of 2 to 11 did not significantly affect the extraction of the analytes by the fiber; therefore no further comparisons with pH adjustments were performed. Although the addition of salt increased the amounts extracted for some analytes, sub μg/l and sub ng/l levels could still be achieved under neutral conditions. Therefore, for the analysis of all eighteen organochlorines combined, the conditions selected for the method are no pH or salt modifications. These conditions may be modified to improve extraction efficiencies if the focus is on a specific analyte or group of analytes. Since this paper concentrates on the combined mixture containing all the target analytes listed, all subsequent analyses using standards were performed under neutral conditions (no salt).

The method precision was determined under neutral standard conditions. A minimum of seven extractions from an aqueous solution with a concentration of 10 ng/ml were performed and analyzed using FID and MS. Similarly seven

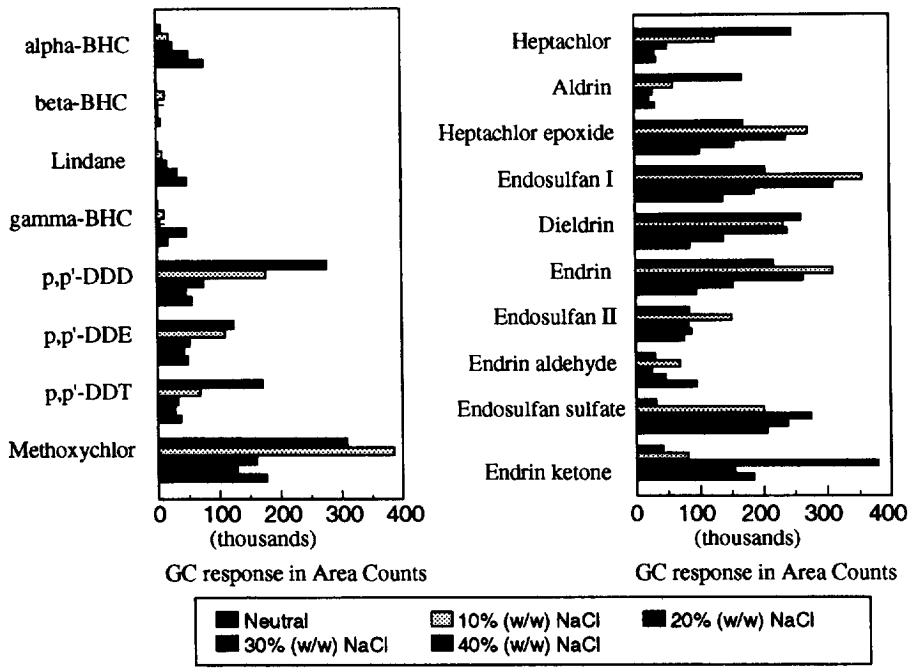

Fig. 2. Effects of different salt concentrations [10–40% (w/w) NaCl] on the extraction efficiency.

extractions of a 1 ng/ml standard aqueous solution were performed and analyzed by ECD. The majority of the eighteen analytes were extracted with precision ranging from 4 to 51% R.S.D. (relative standard deviation) using GC–FID (Varian 6000). The best precision obtained was observed for analyses performed by either GC–ECD (Varian 3400) or MS (Varian Saturn II) where all analytes were extracted with precision between 3 and 20% R.S.D. In general the higher % R.S.D.s were determined for compounds that have equilibration times greater than 90 min such as the DDT group and many of the cyclodienes. The exception is noticed for the BHC compounds which reach equilibrium by 15 min, and still have high % R.S.D.s. The high % R.S.D.s may be attributed to the fact that these analytes are not extracted as efficiently as the other analytes being studied. The extraction of the BHC class of compounds would be improved if a polyacrylate coating was used. The precision of the method was also determined using an autosampler and GC–FID (Varian 3400 CX). The precision calculated for the analytes was within the range of 8–25% R.S.D. These results are comparable or better than the manual SPME injections analyzed using GC–FID. The autosampler being used is a prototype model; therefore it is expected that the % R.S.D. would decrease to a greater extent with the newer model.

The reproducibility between three fibers was found to be very good. Eight extractions from aqueous standards were performed for each of three different fibers using GC–FID (Varian 6000). The R.S.D. of the eight extractions were calculated for each analyte, and fiber. The reproducibility between the fibers was determined by calculating their percent differences. The percent difference for each of the comparisons between fibers was less than 5%. It was not necessary to repeat this analysis by ECD or MS, since reproducibility of the method is not dependent on the detector used. The close agreement between the fibers indicates good reproducibility of the proposed method.

The linearity of the method was tested by FID, ECD, and MS by extracting aqueous standards,

with increasing concentrations, over a range typically between 0.1 and 100 ng/ml, with GC–FID, and 0.001–100 ng/ml using GC–ECD and GC–MS. The response of the detectors in area counts was plotted against the respective concentration to generate calibration curves. The region where the calibration curve was linear was taken as the linear range of the method. The response was linear within the entire range of concentrations analyzed by FID and GC–MS. The maximum concentrations of individual analytes were restricted by their respective solubilities in water. When the concentrations were analyzed using ECD the response from the detector was determined to be linear between 0.001 and 1 ng/ml. The response of ECD between the concentration range of 1 ng/ml to 100 ng/ml is non-linear. Again, the ranges for individual analytes are restricted by their water solubilities. Regression analysis was used to approximate the linearity of the calibration curves generated for each detector.

The linear range experiments provided the necessary information to calculate the detection limits, based on the lowest detectable peak that has a S/N of 3. A typical noise-reading encountered when operating the flame ionization detector fell in a range of 100–300. Therefore based on a noise level of 300 and a signal-to-noise ratio of 3, an area count of 1000 was considered to be an appropriate estimate for the smallest detectable peak. The noise level for ECD was measured prior to every run, and typically had a signal that was equivalent to an area count of 1000. Hence the lowest detectable peak was defined as having an area count of at least 3000. Finally, for the analyses using the mass spectrometer, the signal-to-noise ratio was determined for the area of the quantification mass peak to the noise. At lower concentrations the S/N can be improved by analyzing more than one characteristic mass peak. This would also allow lower detection limits to be achieved by MS. The detection limits calculated based on

Table 2
Detection limits for the US EPA methods compared to detection limits for FID, ECD, and MS coupled with SPME

Pesticide	FID (μg/l)	ECD (μg/l)	MS (μg/l)	Quantitation used for MS	EPA 508[a]	EPA 625[b]
α-BHC	1300	0.9[c]	200	181	25	NA
β-BHC	9000	9[c]	800	181	25	4200
Lindane (γ-isomer)	300	1[c]	200	181	10	NA
δ-BHC	30	2[c]	500	181	10	3100
Heptachlor	50	0.5	3.8	100	10	1900
Aldrin	160	0.9	4.5	263	75	1900
Heptachlor epoxide	20	0.4	0.2	351	15	2200
Endosulfan I	2	0.3	0.6	241	15	NA
p,p'-DDE	8	0.1	0.6	235	20	5600
Dieldrin	80	0.3	0.06	318	10	2500
Endrin	20	0.2	0.5	263	25	NA
Endosulfan II	30	0.4	0.3	159&195	15	NA
p,p'-DDD	10	0.06	0.02	246	2.5	2800
Endrin aldehyde	350	4.7	0.5	345	24	NA
Endosulfan sulfate	90	0.05	4.5	272	15	5600
p,p'-DDT	7	0.3	0.08	235	60	2700
Endrin ketone	81	0.5	0.6	317	NA	NA
Methoxychlor	8	1.6	0.03	227	50	NA

[a] According to Ref. [4].
[b] According to Refs. [4,5].
[c] 30% (w/w) NaCl added to the solution.
NA = not analyzed by methods.

these concentrations are listed in Table 2. The detection limits achieved using GC–FID (Varian 6000) for some analytes were comparable to the detection limits required by the EPA 508 and 625 methods [2–5]. This is primarily due to the large amount of analyte that is extracted by the fiber and the sensitivity of FID toward these compounds. However, an increase of approximately

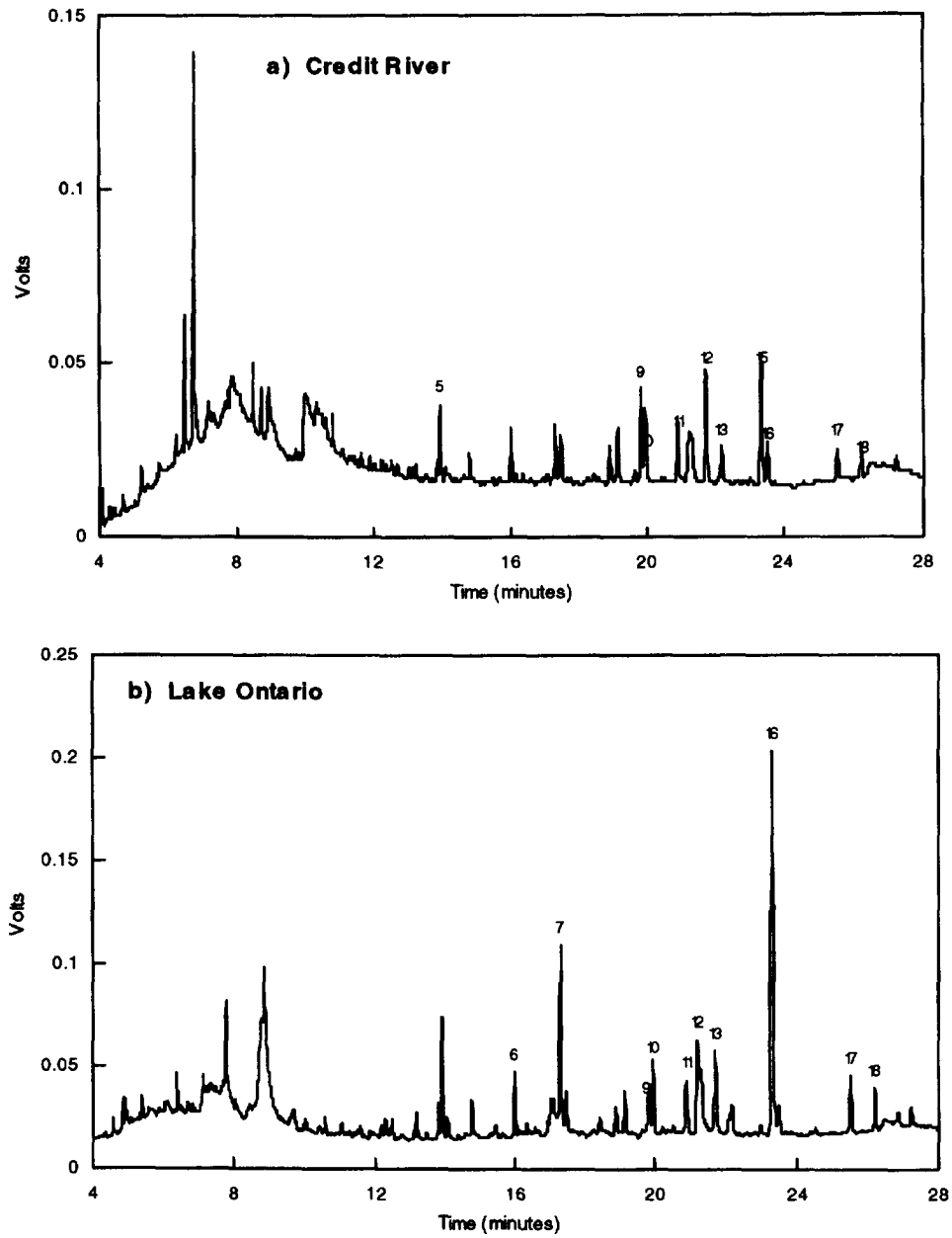

Fig. 3. Qualitative analysis of water samples taken from the Credit River and Lake Ontario by SPME–GC–ECD. Peaks: (a) 5 = heptachlor, 9 = dieldrin, 10 = *p,p'*-DDE, 11 = endrin, 12 = endosulfan II, 13 = *p,p'*-DDD, 15 = endosulfan sulfate, 16 = *p,p'*-DDT, 17 = endrin ketone, 18 = methoxychlor; (b) 6 = aldrin, 7 = heptachlor epoxide, 9 = dieldrin, 10 = *p,p'*-DDE, 11 = endrin, 12 = endosulfan II, 13 = *p,p'*-DDD, 16 = *p,p'*-DDT, 17 = endrin ketone, 18 = methoxychlor.

two orders of magnitude is seen when using more sensitive and selective detector equipment such as ECD or MS.

The SPME method developed was successfully applied to the analysis of environmental samples. GC–ECD was used to perform the analysis, since this detector was much more selective to the analytes of interest than FID and fiber interference (sometimes seen when using GC–MS) was eliminated. The method was applied to river and lake samples, as well as Arctic snow and ice samples. The river and lake samples were initially analyzed by both standard addition and external calibration. The results were similar for both quantitation methods; therefore all further analyses were completed using only external calibration quantitation. Fig. 3 illustrates the qualitative extraction of the lake and river samples. The Arctic samples were initially analyzed using GC–ECD (Varian 3400) with one column (PTE-5). Fig. 4 illustrates the presence of organochlorines in the sample. Since only one column was used, there was no confirmation that the responses observed were caused by organochlorine pesticides and not PCBs or other chlorinated species that may be present in the sample. Therefore, the analysis of the Arctic samples was repeated using a dual column with dual ECD detection. Using two columns of different polarities provided a confirmation of the identity of analytes detected in the sample by the single-column method. Since the environmental samples were similar in nature to pure water there was no sample preparation or matrix modification necessary. The quantitative results are illustrated in Table 3.

4. Conclusions

This paper has outlined the successful development of a method based on the SPME technique for the analysis of organochlorinated pesticides from aqueous samples. The method is precise,

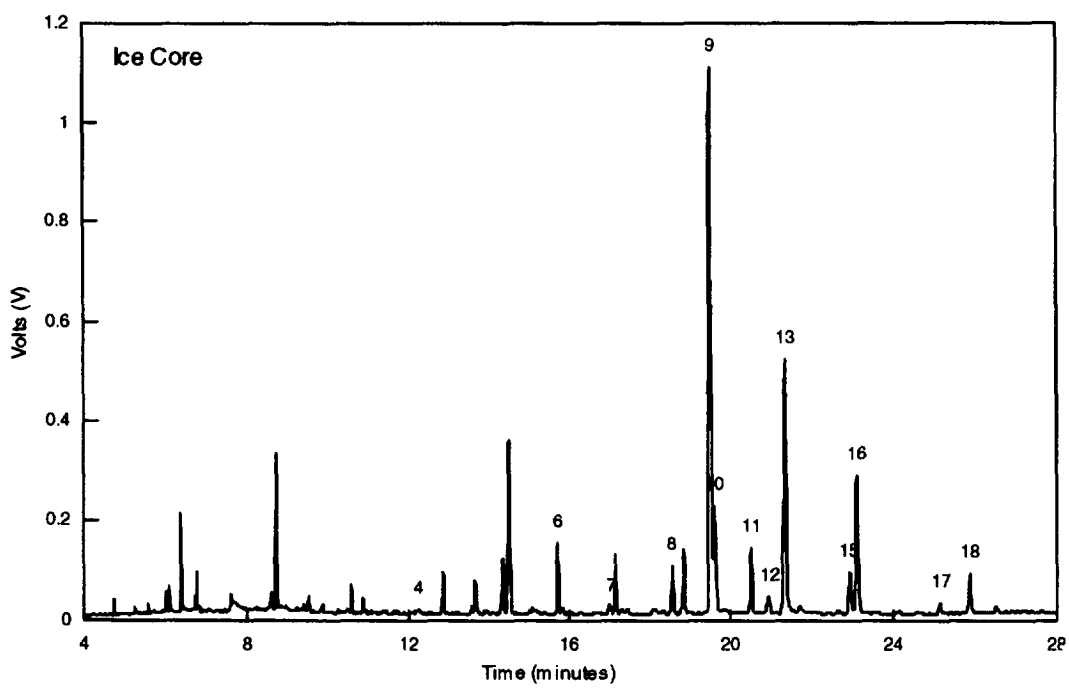

Fig. 4. SPME–GC–ECD of an ice core sample from the Arctic regions of Canada. Peaks: 4 = δ-BHC, 6 = aldrin, 7 = heptachlor epoxide, 8 = endosulfan I, 9 = dieldrin, 10 = *p,p'*-DDE, 11 = endrin, 12 = endosulfan II, 13 = *p,p'*-DDD 15 = endosulfan sulfate, 16 = *p,p'*-DDT, 17 = endrin ketone, 18 = methoxychlor.

Table 3
Organochlorines detected in Canadian Arctic samples

Pesticide	Field samples	
	Ice core (μg/l)	Surface snow (μg/l)
α-BHC	not detected	not detected
β-BHC	not detected	not detected
Lindane (γ-isomer)	not detected	not detected
δ-BHC	44	295
Heptachlor	not detected	not detected
Aldrin	52	185
Heptachlor epoxide	28	68
Endosulfan I	31	136
p,p'-DDE	42	133
Dieldrin	80	470
Endrin	35	220
Endosulfan II	22	101
p,p'-DDD	105	499
Endrin aldehyde	not detected	180
Endosulfan sulfate	28	80
p,p'-DDT	188	333
Endrin ketone	46	203
Methoxychlor	71	443

reproducible and linear over a wide range. The detection limits obtained for the SPME method using either ECD or MS are comparable, if not better than those required by US EPA methods 508, and 625 respectively. The SPME technique developed has been shown to be a viable, rapid alternative for the quantitative and qualitative analysis of organochlorines from aqueous environmental samples. The compact nature of the sampling device and the elimination of solvents allows SPME to be easily adapted for automation and provides an opportunity to perform on-site field sampling studies.

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