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New fast screening method for organochlorine pesticides in water by using solid-phase microextraction with fast gas chromatography and a pulsed-discharge electron capture detector

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A new fast screening method has been developed for the analysis of organochlorine pesticides in water that takes less than 10 min to perform and has detection limits of the order of 10 ng l^{-1}. Pesticide extraction was achieved by solid-phase microextraction and the separation was performed using a micro-bore (0.1 mm) capillary column. A laboratory-built cryotrap system was used to focus the analytes prior to introduction to the column and a pulsed-discharge electron capture detector enabled sensitive, selective measurements of the pesticide peaks to be made. The 100 μm polydimethylsilicone (PDMS) coated fibre gave better recoveries than the 30 or 7 μm film PDMS fibres and an inter-fibre study comparing three 100 μm film fibres showed good reproducibility. With extraction times of 2 min, the procedure was found to be linear over the range 0.01–1.2 ng ml^{-1}. The procedure was tested with a real river water sample.

Keywords: *Solid-phase microextraction; organochlorine pesticides; fast gas chromatography; pulsed-discharge electron capture detector; carbon dioxide cryotrap*

The need for speed in environmental sampling is ever increasing. The relatively slow methods of analysis currently being used in environmental laboratories restrict the number of analyses possible per day. The analysis of environmental contaminants such as organochlorine pesticides (OCPs) in aqueous samples is of particular concern and can be achieved by using a variety of methods.[1] Liquid–liquid extraction (LLE) is the most commonly used method for extracting OCPs from aqueous samples and can take over 12 h to perform.[1,2] Recently liquid–solid extraction (LSE)[3,4] has gained favour as a replacement for LLE. Both these procedures often require a concentration step involving solvent evaporation, which may lead to a loss of the more volatile analytes in the mixture or to the concentration of interfering compounds.

Solid-phase microextraction (SPME) is a new method of sample preparation; it is quick, requires no solvents and is easily automated.[5,6] The SPME device and methodology are described in detail elsewhere.[5–10] SPME has proved to be effective in extracting OCPs from aqueous matrices and is easily interfaced with conventional GC systems. Attempts have been made to try to improve the extraction efficiencies for the OCPs under observation, including 'salting out' the pesticides,[7–9] altering the pH of the sample matrix[7] and headspace *versus* direct sampling.[8–10] In general, adequate detection limits can still be achieved without any modifications to the sample matrix, particularly when a sensitive detection method such as electron capture is feasible.

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In SPME, extractions are typically performed for a length of time that nears the equilibrium time of the component in the sample with the longest equilibrium time. Long extraction times such as these are used in an effort to improve the detection limits and precision of the technique. Equilibrium times quoted for OCPs vary from study to study, but fall in the range 30–180 min.[7,9] Two studies have shown that linear responses having good precision are possible by using extraction times well short of equilibrium times.[5,11] This technique is also called non-equilibrium SPME. If sensitive detection is feasible then a reduction in extraction time and a consequent reduction in analysis time is possible with non-equilibrium SPME. Non-equilibrium SPME was used in this study to further reduce the sample preparation time.

Fast GC, introduced in 1965 by Desty,[12] is also employed to reduce the separation time of the analytes. Typical methods of separation for OCPs use a 30 m × 0.25 mm id column giving separation times of the order of 25–35 min.[7–10] Schutjes *et al.*[13] separated a mixture of OCPs in under 12 min by using a 4.1 m × 55 μm id fused silica capillary column, proving that fast GC of the OCPs is possible with narrow-bore columns. This hypothesis was later confirmed by Shirey,[14] who combined SPME with fast GC to achieve a separation time around 15 min and a total analysis time of about 40 min.

A major problem with interfacing SPME and conventional GC is the introduction of the analytes on to the column as a narrow plug. Analytes desorb relatively slowly from the SPME fibre, which causes peak tailing before the analytes enter the column. Real-time analyses of some hydrocarbons and aromatic hydrocarbons desorbing from SPME fibres have shown desorption times to be in the region 12–60 s.[15,16] An inverse relationship between temperature and desorption time was found. Different methods have been investigated to try to minimise peak broadening and tailing. These include internally heated fibres,[17] cryogenic trapping[16] and cool initial oven temperatures.[14,16] A cool initial oven temperature is the method usually used to refocus the analytes at the head of the column because no modifications are required to the GC system and the oven is easily controlled. However, cool initial oven temperatures increase the analysis time. In this study, a laboratory-built carbon dioxide cooled cryotrap system[18] was used to refocus the analytes after the initial desorption from the SPME fibre.

The combined use of cryotrapping with resistive heating is a common technique in fast GC due to the requirements for a narrow bandwidth entering the column.[19,20] The analytes are reintroduced when desired by using direct resistive heating. A cryotrap has the advantage of being able to focus the analytes at temperatures as low as −60 °C (with CO_2 or cooler with liquid N_2) while the oven temperature is independently controlled. The oven can, therefore, be held at the optimum initial separating temperature at the time of sample introduction. this enables the chromatographic run time to be kept the same in SPME as for conventional liquid injections.

A pulsed-discharge electron capture detector (PDECD) developed in recent years by Wentworth and co-workers[21,22] has proven to perform comparably with conventional radioactive (^{63}Ni) ECDs for OCPs. The PDECD does not require a radioactive source, but instead uses pulses of high voltage electricity to generate a helium plasma. There are, therefore, no concerns with radiation monitoring or disposal of radioactive materials. This study combined non-equilibrium SPME, fast GC (with a modified inlet system) and a PDECD in the development of a new fast screening method for the analysis of OCPs in water samples.

Experimental

Reagents

A pesticide calibration mix (1 to 400 ng ml^{-1} in isooctane) was purchased from Radian International (Austin, TX, USA). Individual pesticides for peak identification were also acquired: tetrachloro-*m*-xylene (TCMX), *cis*-chlordane, *trans*-chlordane, *p*,*p*′-DDE (Supelco, Bellefonte, PA, USA) and *p*,*p*′-DDD (Radian) were all purchased as the pure compound. Endrin, endrin ketone, endosulfan sulfate, α-benzene hexachloride (BHC), δ-BHC (all 1000 μg ml^{-1} in methanol), β-BHC (1000 μg ml^{-1} in acetone) and endrin aldehyde (1000 μg ml^{-1} in hexane) were all purchased from Radian. All solvents used were HPLC grade unless otherwise stated. Solvents used were methanol, isooctane (2,2,4-trimethylpentane) and ACS analytical grade hexane (Fisher Chemicals, Fairlawn, NJ, USA), acetone (EM Science, Gibbstown, NJ, USA) and ultrapure, distilled deionised (18.2 MΩ) water obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA). All glassware was deactivated prior to use with dimethyldichlorosilane (Supelco) as described by the manufacturer. All gases were supplied by Pallini Industries (Athens, OH, USA).

Sample preparation

Initial stock solutions of TCMX and *cis*- and *trans*-chlordane were prepared to 64, 68 and 64 μg ml^{-1}, respectively, in methanol. Stock solutions of *p*,*p*′-DDE and *p*,*p*′-DDD were prepared to 52 and 48 μg ml^{-1}, respectively, in hexane. A surrogate stock solution containing the ten pesticides at 1 μg ml^{-1} was prepared in methanol from the individual stock solutions. The pesticides α- and δ-BHC and *cis*- and *trans*-chlordane were diluted to half the relative concentration of the other pesticides due to the response factor of the detector to each pesticide. Working spiking solutions were prepared in concentrations ranging from 5 to 600 ng ml^{-1} by diluting the surrogate stock solution with methanol. For each working spike solution 50 μl was diluted to 25 ml with purified water to obtain a range of spiked water samples from 0.01 to 1.20 ng ml^{-1}.

A river water sample was collected in a 1l reagent bottle from the bank of the Hocking River in Athens, OH and was filtered prior to analysis. All organic based solutions were stored in a freezer and all water based solutions stored in a refrigerator. Solutions were allowed to warm to room temperature before use.

Instrumentation

A Varian 3400 GC oven equipped with an injector capillary conversion kit (SGE, Austin, TX, USA) was used in all experiments. The split/splitless injection port was held at 250 °C. Ultrapure helium (99.999%) was the carrier gas with a flow rate of 1.8 ml min^{-1}. The septa used were thermal green septa (Alltech, Deerfield, IL, USA). Hydrocarbon traps, oxygen traps and moisture traps were used in-line (Alltech). The detector was a PDECD detector (Valco Instruments, Houston, TX, USA) used in the ECD mode at 330 °C. Attenuation was set at 1 and data was collected with an analogue to digital converter at 30 Hz using EZChrom software (6.5, Scientific Software, CA, USA). The plasma was formed by helium purified with an in-line gas purifier (Valco) at a flow rate of 30 ml min^{-1}. The dopant gas, also purified with in-line moisture and oxygen traps, was 5% methane in helium at a flow rate of 2.45 ml min^{-1}.

A laboratory-built, carbon dioxide cooled, resistively heated cryotrap system was used to focus the analytes prior to introduction to the column. The cryotrap was positioned between the injection port and the separation column. Fig. 1 shows a simplified diagram of the apparatus used, which is described in more detail in previous work.[18] The power supplies for reheat were from a STACO 3PN501 unit, BK precision 1653 ac power supply and a Widjever transformer, all commercially available. The power supply was connected to the metal tubing with insulated copper wire. Copper tubing was crimped around the metal tubing and the ends of the copper wire at either end of the cryotrap to enhance the electrical contact. A type J fine gauge thermocouple (Omega, Stamford, CT, USA) coupled to a digital indicator (Omega) was used to measure the reheat temperature. The metal tubing used was obtained from Quadrex (New Haven, CT, USA) and had an id of 0.25 mm. The 20 cm lengths of metal tubing were cleaned before use by forcing 5 ml acetone followed by 5 ml hexane through with compressed nitrogen. The tubing was purged for a further 2 min with nitrogen before installation in the GC oven. The metal tubing was then conditioned for 2 h at 300 °C with a low helium flow. An MXT low-dead-volume connector (Restek, Bellefonte, PA, USA) was used to connect the metal tubing to the separation column, which was a Quadrex 5 m × 0.1 mm id × 1 μm film thickness bonded methyl 5% phenyl silicone column.

After some initial studies, the following methodology was adopted for liquid injections. Injections of 1 μl were made with the split flow at 18 ml min^{-1}. The cryotrap was held at 60 °C and the oven held at 220 °C for 0.2 min. At 0.2 min the CO_2 was turned off, the discharge applied and the oven temperature was ramped to 266 °C at 20 °C min^{-1}. The cooling and reheat systems were controlled by using EZChrom software. A study at room temperature showed the reheat system raised the temperature of the metal tubing an average of 290 °C (RSD = 4%, n = 20).

SPME

All fibres (Supelco) used had polydimethylsiloxane coatings that were bonded or coated depending on film thickness. Before use, the 30 and 100 μm film coated fibres were conditioned for 1 h at 250 °C and the 7 μm bonded film fibre was conditioned for 2 h at 320 °C. During extraction, samples were contained in 2 ml silanized amber vials sealed with hole caps and Teflon faced silicone septa. Small volume vials were used to minimise

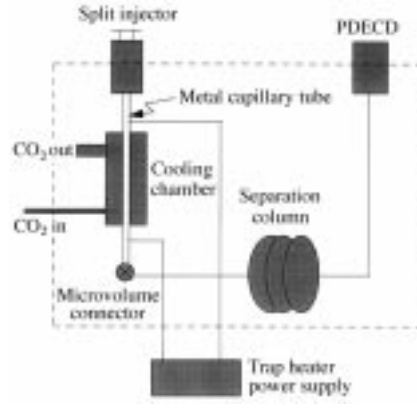

Fig. 1 Schematic representation of the experimental layout.

the hazardous waste produced during method development and to demonstrate the sensitivity of the method with small sample sizes. To agitate the solutions, Teflon-coated magnetic stir bars (8 mm × 1.5 mm) on a Magnestir (Van Waters and Rogers, Lab Line Instruments, Melrose Park, Illinois, USA) magnetic stirrer were used. An extraction time of 2 min and a desorption time of 2 min were used throughout. After extraction, the fibre was immediately transferred to the hot injection port. For the first 2 min of desorption, the injection port was in splitless mode, the cryotrap at 60 °C and the oven at 220 °C. At 2 min, the fibre was removed and the split flow opened to 18 ml min^{-1}. At 2.3 min, the CO_2 cooling was turned off, the discharge applied and the oven temperature ramped to 266 °C at 20 °C min^{-1}.

Results and discussion

Cryotrap and PDECD characterization

Preliminary work with liquid injections was performed to characterise the cryotrap and the PDECD. On observing the digital readout from the thermocouple inside the cryotrap, it could be seen that the trapping temperature was not constant. The on/off valve that controlled the CO_2 flow had a limited minimum opening time, which allowed more CO_2 into the cryotrap than was necessary to maintain a constant temperature. With a full cylinder of CO_2 and the trapping temperature set at 60 °C, the temperature inside the trap varied from 60 to −10 °C in any one valve opening. The reheat system could not be adjusted quickly enough to compensate for the variations in trapping temperature. For this reason, the final reheat temperature ranged from 280 to 350 °C depending on the metal tubing temperature at the time of discharge. This variation did not affect the peak widths in the resulting chromatograms.

Endrin decomposition was evident during peak identification. A simultaneous decrease in endrin peak height and the appearance of two initially unidentified peaks was observed. It is well known that endrin is susceptible to decomposition at elevated temperatures and with active media present.[23,24] The breakdown products are endrin aldehyde and endrin ketone and were identified by injection of the single components. The percentage decomposition was calculated[24] under various conditions to locate the region of endrin breakdown. This showed that endrin was decomposing in both the injection port and in the metal tubing. Ten replicate injections of endrin at 50 ng ml^{-1} were made with trapping and reheat applied and again with trapping and no reheat. The results are given in Table 1. Applying the reheat was found to significantly increase the extent of endrin breakdown compared to the injection port alone. Even the temperature of the injection port alone caused more than the maximum decomposition limit set by the US Environmental Protection Agency (EPA).[24] This method states that 'corrective action' should be taken if total endrin breakdown exceeds 20%. Deactivation of the injection port liner with dimethyldichlorosilane significantly reduced the decomposition but the total breakdown could not be consistently kept below 20%. The deactivation process did not appear to have a permanent effect so it was repeated every 3–4 weeks throughout the study. Evidence also suggests that the metal tubing loses its inertness over time. Endrin decomposition increased more over the two week period with reheat than without reheat. For this reason the tubing was replaced approximately every 450 reheats. The decomposition was not a great concern as the peak from one of the endrin decomposition products, endrin aldehyde, elutes well resolved from any of the other peaks (Fig. 2). A peak observed at the retention time corresponding to endrin aldehyde could serve as an indication that the sample originally contained endrin. A confirmatory study would have to be performed in any case as this method is proposed as a screening technique.

Endrin decomposition was higher with the SPME studies when compared to liquid injections as the analytes spend more time in the injection port and have increased exposure to the active sites present. The use of a smaller volume liner for SPME or inlet pressure (flow) programming for liquid injections[23] could be used to combat the breakdown problems. In both cases the residual time the analytes spend in the injection port would be reduced, and so would be expected to reduce sample decomposition.

The best responses for the PDECD were obtained at the maximum operating temperature of 330 °C and with gas flows as detailed in the experimental section. The gas flows corresponded closely to those recommended by the manufacturer. Method development with the PDECD (data not shown) was time consuming because the detector had to be cooled to below 70 °C before the flow rates of the plasma gas and dopant gas could be measured. Once the detector was optimised, the background current remained stable at 1.2 V with a noise of roughly 0.4 mV.

Liquid injections

Fig. 2 shows a chromatogram obtained of the ten pesticides at the 100 ng ml^{-1} level. It can be seen that 10 of the 11 components were successfully resolved in less than 2.5 min. Peak identification was made by using injections of the single component solutions under identical conditions. The oven temperature could be altered to resolve the co-eluting DDD–endrin peak, but at a significant loss to analysis time. Because this is a screening technique, any positively identified peaks would have to be confirmed with another procedure, therefore, the co-elution observed was deemed acceptable when taking into account the time saved with the oven conditions used. A calibration curve was produced from duplicate injections of solutions from 0.1 to 400 ng ml^{-1}. Table 2 gives the correlation coefficients and limits of detection (LOD) obtained from the linear plots. As can be seen, the LOD in this study compare well with those of a previous study on chlorinated pesticides with

Table 1 Results of endrin decomposition study showing percentage decomposition* (%RSD) (n = 10)

	With reheat	Without reheat
Before deactivation of injection port liner	31(11)	28(9)
After deactivation	23(23)	15(24)
Two weeks after deactivation	49(23)	25(34)

* Calculated according to ref. 24.

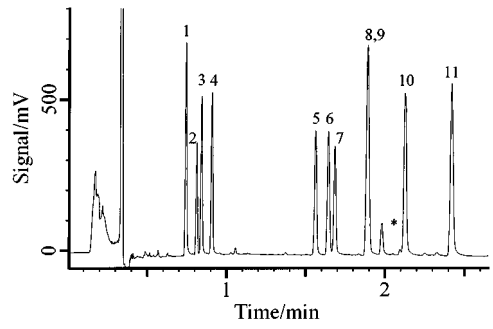

Fig. 2 A chromatogram obtained from a 1 µl injection of a standard pesticide calibration mix at the 100 ng ml^{-1} level. Split ratio was 10 : 1. Peaks: 1 = TCMS, 2 = α-BHC, 3 = β-BHC, 4 = δ-BHC, 5 = *cis*-chlordane, 6 = *trans*-chlordane, 7 = *p,p′*-DDE, 8 = *p,p′*-DDD, 9 = endrin, 10 = endosulfan sulfate, 11 = endrin ketone, * = endrin aldehyde.

this detector. The two lowest r^2 values are for the *p,p′*-DDD–endrin peak and endrin ketone. The reduced linear response of these two peaks was attributed to the co-elution of *p,p′*-DDD and endrin and the variation of endrin decomposition.

SPME results

Initial method development was carried out with the 100 μm fibre. Various extraction and desorption times were tested to minimise the entire SPME procedure time while still maintaining adequate detection limits. An extraction time of 2 min and a desorption time of 2 min were adequate to identify all the pesticides present. The exception was decachlorobiphenol (DCBP), an internal standard, which has a significantly longer elution time than the other analytes in the mixture and is poorly extracted by the SPME fibre with the short absorption time used. For this reason the commercially available pesticide calibration mix was reproduced with the DCBP omitted.

A study to optimise the volume of sample to be extracted was performed. In Fig. 3 the average peak heights (n = 4) for three pesticides were calculated and plotted against the volume of water sample extracted. Performing extractions from 1 ml (a headspace extraction because the fibre was not submerged in solution) gave very small recoveries. The smaller recoveries observed are not surprising if one considers the processes involved in extracting the semi-volatile pesticides. The analytes have to partition between the sample matrix and the headspace and between the headspace and the fibre coating. The net result is a reduced mass extracted at equilibrium and a longer time to reach equilibrium. Extracting from a vial that was completely full (1.95 ml) also gave small recoveries. It was assumed that without the formation of a vortex in the solution, efficient stirring of the sample could not take place and mass transfer in the sample matrix became the limiting factor. The fibre was positioned in the vortex and so the vortex constantly brought fresh solution to the fibre surface. The optimum volume was found to be 1.7 ml, with the fibre submerged in the sample during extraction. The needle of the SPME syringe remained in the small headspace in the vial to prevent wicking of the sample during extraction.

Fig. 4(*a*) shows a chromatogram obtained from a 0.2 ng ml^{-1} solution using a 100 μm coated film fibre. As can be seen, the total desorption and separation time is less than 4.5 min. Peak identification was achieved by overlapping chromatograms obtained by direct injections with those obtained by SPME. A baseline shift of 2.1 min (which is the difference in trapping times) overlaid the pesticide peaks exactly.

Many extraneous peaks are observed throughout the chromatogram, which were attributed to septum bleed. A blank run [Fig. 4(*b*)], with no injection or desorption of a fibre, yielded virtually all the extraneous peaks. None of the extraneous peaks was found to elute at a retention time equal to that of any of the pesticides but the instability of the baseline meant that the LOD increased. More thermally stable septa were tested to try to reduce septum bleed, but were prone to leaking after only a few SPME injections so their use was discontinued. The use of a septumless injection port could solve the problems incurred with septa.

Film thickness

Initial work with SPME was carried out to determine which coating worked best in a non-equilibrium situation. Triplicate extractions were performed with each film thickness to determine which gave the best response. Solutions at 0.2

Table 2 Results of a calibration curve with duplicate liquid injections and a comparison with LOD obtained in other work. 1 μl Injections, split ratio of 10 : 1, range = 0.1–400 ng ml^{-1}

	r^2	LOD/fg on column	Cai *et al.**
α-BHC	0.998	13	34
β-BHC	0.991	50	83
δ-BHC	0.993	25	N/A
cis-Chlordane	0.991	13	N/A
trans-Chlordane	0.992	13	N/A
p,p′-DDE	0.996	50	50
p,p′-DDD–endrin	0.968	10 + 10†	70 + 84
Endosulfan sulfate	0.990	50	N/A
Endrin ketone	0.984	25	N/A

* Values taken from ref. 22. † Values estimated due to co-elution of pesticides. N/A = peaks not analysed in this method.

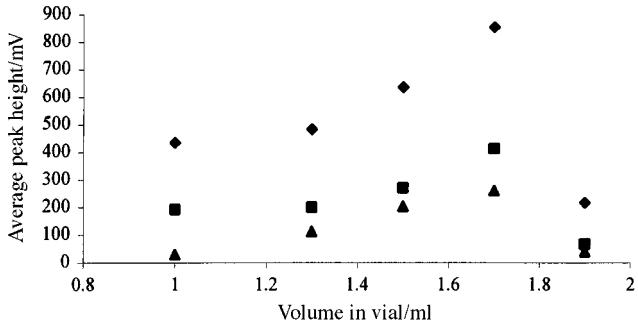

Fig. 3 Plots to show how peak heights vary with volume of solution contained in the 2 ml vial. ◆, *cis*-Chlordane; ■, *p,p′*-DDD; ▲, endosulfan sulfate.

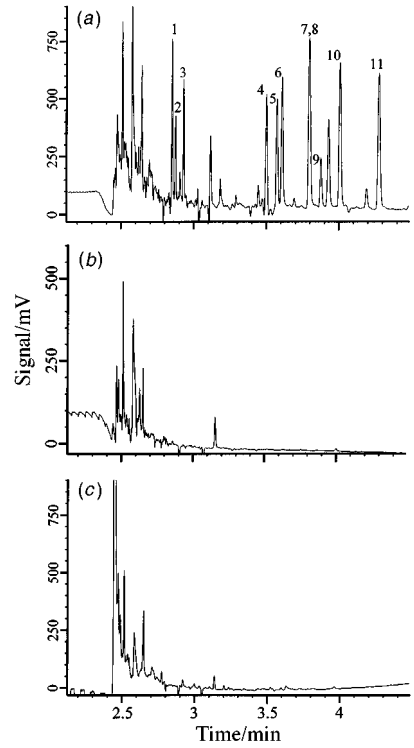

Fig. 4 Chromatograms obtained after 2.3 min trapping at 60 °C. (*a*) SPME fibre desorbed for 2 min after a 2 min extraction of a 0.2 ng ml^{-1} spiked water sample. Peaks: 1 = α-BHC, 2 = β-BHC, 3 = δ-BHC, 4 = *cis*-chlordane, 5 = *trans*-chlordane, 6 = *p,p′*-DDE, 7 = *p,p′*-DDD, 8 = endrin, 9 = endrin aldehyde, 10 = endosulfan sulfate, 11 = endrin ketone. (*b*) Blank run showing the extraneous peaks caused by septum bleed being focused by the cryotrap. (*c*) SPME of Hocking River water; no pesticide peaks observed.

ng ml^{-1} extracted with the 30 μm film fibre showed significantly smaller peaks than the 100 μm fibre. Extractions with the 7 μm fibre gave no pesticide peaks. The 100 μm fibre has a larger surface area in contact with the sample matrix than the 30 and 7 μm fibres. Surface areas were calculated to be 9.8, 5.4 and 3.9 mm^2 for the 100, 30 and 7 μm fibres, respectively, assuming a fused silica fibre length of 10 mm and diameter of 110 μm.[8] It is thought that with such a short extraction time, the larger surface area of the 100 μm fibre allowed a faster partitioning of the pesticides into the coating. The smaller surface area and possible irreversible adsorption of the pesticides to active sites on the silica fibre[16,25] may account for the lack of peaks observed for the 7 μm fibre. Owing to the larger recoveries of the 100 μm fibre, this film thickness was used exclusively throughout the following studies.

Carryover

Carryover was tested for by repeating the desorption step after a typical extraction and desorption of a 0.2 ng ml^{-1} solution. a small degree of carryover was observed on a second desorption but not on a third analysis. Between subsequent extractions, a cleaning procedure of desorbing the fibre for 3 min at 250 °C and cooling for 2 min at room temperature was adopted. This step could easily be accommodated off-line in a syringe type apparatus to free the GC instrument for another analysis.

Calibration curve

A calibration curve was produced using spiked water samples from 0.01 to 1.2 ng ml^{-1} under the conditions described previously. Before sealing the caps on the vials, a 5 μl aliquot of 64 ng ml^{-1} TCMX was added as an internal standard (at 1.9 ng ml^{-1}). Taking the ratio of the peak heights to that of the internal standard (TCMX) for each pesticide did not improve the precision of the linear plots so TCMX was not used in subsequent work. The curves became clearly non-linear above 0.4 ng ml^{-1}. The results for the linear plots, absolute peak height from 0.01 to 0.4 ng ml^{-1} are given in Table 3. Considering the short extraction time used, LOD (defined as a peak giving a response equal to a blank signal plus three times the noise) compare well with results published in previous work[7,9] and with those set by the EPA.[24,26] Some of the r^2 values are rather low. Upon close examination this was found to be because for some of the pesticides even 0.4 ng ml^{-1} was above the true linear range.

Several calibration curves were produced over a period of five weeks. For each calibration curve produced, the average retention times were calculated for each peak. Retention times varied less than 0.25% in any one day, and less than 2% over the period of five weeks. The excellent precision of retention times was attributed to the strictly controlled introduction of the pesticides by the computer and reheat system.

Table 3 Results of the calibration curve obtained by SPME extractions over the range 10–400 ng l^{-1}

	r^2	LOD/ ng l^{-1}	From literature[7]	From literature[9]	EPA 508[24]
α-BHC	0.992	10	900	1	25
β-BHC	0.980	20	9000	1	10
δ-BHC	0.965	20	2000	2	10
cis-Chlordane	0.978	5	N/A	N/A	1.5
trans-Chlordane	0.969	5	N/A	N/A	1.5
p,p′-DDE	0.908	10	100	1	10
p,p′-DDD–endrin	0.969	10 + 10*	60 + 200*	0.1 + 1*	2.5 + 15*
Endosulfan sulfate	0.929	10	50	0.6	15
Endrin ketone	0.964	10	500	1	N/A

* Respective LOD for *p,p′*-DDD and endrin. Values obtained in this study are estimates based on co-eluted peaks obtained. N/A = not analysed.

Inter-fibre study

A comparison between three 100 μm fibres was carried out to determine inter-fibre reproducibility. A minimum of five extractions was performed for each fibre. The mean peak height and RSD were calculated for every peak for each fibre. A *t*-test was performed between the mean peak heights for each peak with each fibre, to determine if there was a significant difference [at 95% confidence level (CL)] between the means. Six of the 27 tests failed: fibre 3 was significantly different from the other two fibres for the α-BHC and δ-BHC peaks, fibres 1 and 2 were significantly different for the *p,p′*-DDD–endrin peak, and fibres 1 and 3 failed the *t*-test for the endrin ketone peak. The spiked sample used for this study was contained in a 25 ml calibrated flask, and the 1.7 ml aliquots transferred to the vials roughly 1 h before sampling. The more volatile pesticides (*i.e.* α-, β- and δ-BHC) could have partitioned into the headspace of the calibrated flask and diffused out each time the stopper was removed. This could have significantly reduced the quantity of the more volatile components, so leading to the results observed. The varying degree of endrin decomposition was considered to be the reason for the failed tests for the *p,p′*-DDD–endrin and endrin ketone peaks.

River water analysis

Triplicate analyses of the Hocking River water sample did not give any positive pesticide identification peaks as shown in Fig. 4(*c*). Chlorinated pesticide peaks were not expected in the river water sample and the river water was then used to examine the effect of organic matter on extraction. Samples of Hocking River water and purified water were spiked to the same concentration (0.2 ng ml^{-1}). They were tested 1 h after spiking and again after 50 h to see if organic or particulate matter in the river water affects the amount of pesticides extracted. The results for percentage recoveries are given in Table 4 along with the per cent. RSD for each peak. A *t*-test (95% CL) was performed for each peak between the two aqueous solutions to see if the percentage recoveries were different. There were no significant differences between the two samples when analysed the same length of time after spiking. It appears that the average recoveries decrease over the period of 50 h. The only significant decreases found were for α- and δ-BHC and for *p,p′*-DDE. A loss in recovery over a 50 h time period is not unusual, as demonstrated by previous work with aromatic hydrocarbons.[25] RSD values for per cent. recoveries averaged just less than 20%. RSD values are clearly larger for the spiked river water than the spiked purified water samples. The percentage recovery was determined by comparing peak areas obtained by SPME with the linear plots obtained from the standard liquid injection calibration curves. Possible sources of error are the discrimination phenomenon in liquid standard injection into a split splitless injector introducing error in calibration. Another problem could be an uneven distribution of organic matter in the river water. The use of a suitable internal standard should reduce the RSD.

The mass extracted by SPME was expressed as a percentage of the absolute mass contained within the vial before extraction. The values obtained for percentage recoveries are expectedly low if one considers the short extraction time used compared with the time for equilibrium to be established. It should be noted that the percentage recovery represents the amount recovered at the detector, as some analytes are flushed out of the injection port after 2 min desorption, and some remain on the fibre as carryover. Table 4 also gives the estimated and actual

Table 4 Percentage recoveries obtained from SPME extractions of water samples spiked to 0.2 ng ml^{-1} (% RSD) (n = 5)

	Purified water after 1 h	Hocking water after 1 h	Purified water after 50 h	Hocking water after 50 h	Estimated concentration*/ ng ml^{-1}	Actual concentration/ ng ml^{-1}
α-BHC	2.0(12)	1.3(25)	1.6(40)	1.6(29)	0.08	0.1
β-BHC	0.7(31)	0.8(24)	0.8(32)	0.7(27)	0.18	0.2
δ-BHC	1.2(17)	1.5(27)	1.3(18)	1.3(27)	0.1	0.1
cis-Chlordane	2.7(7)	3.0(15)	1.8(6)	2.2(31)	0.14	0.1
trans-Chlordane	3(5)	3.3(19)	1.9(10)	2.2(29)	0.13	0.1
p,p′-DDD	2.4(9)	2.4(16)	1.0(10)	1.5(21)	0.21	0.2
p,p′-DDD–endrin	1.9(18)	1.9(18)	1.4(13)	1.4(13)	0.2	0.2
Endosulfan sulfate	2.2(21)	2.5(24)	2.0(20)	1.8(26)	0.19	0.2
Endrin ketone	2.8(5)	2.8(26)	2.1(2)	2.3(26)	0.23	0.2

* Values were calculated using the peak heights obtained from purified water 1 h after spiking and the linear plots obtained in Table 3.

concentrations of the pesticides in purified water 1 h after spiking. Values for the estimated concentration were obtained by comparing the peak heights from the recovery study to the linear plots obtained from the calibration curve in Table 3. As can be seen, there is a very close correlation between the estimated and actual concentrations. This demonstrates the consistency of the technique and confirms the use of an external standard calibration curve as an adequate method for determining the concentration of pesticides in an aqueous sample.

Conclusion

This work shows the possibility of very fast environmental sampling by using modified equipment found in a typical analytical laboratory. A total analysis time for extraction, separation and measurement of less than 10 min was achieved and resolution was obtained for nine out of the ten pesticides used in this study. A calibration curve showed that the technique is linear over two orders of magnitude, and can detect pesticides below the maximum contamination levels set by the US EPA. LOD were affected by septum bleed, which could possibly be eradicated with the use of a septumless injection port. Endrin decomposition could not be kept below the minimum requirement of 20% (as set by the US EPA). A decomposition product, endrin aldehyde, eluted well resolved from any of the other peaks and could serve as an indication that the sample originally contained endrin. A confirmational analysis such as by GC–MS would be required to verify any positive identification peaks and quantify the results. The development of a cryotrap with a more stable trapping temperature should help reduce this decomposition and will be reported on at a later date. The reheat temperature could then be minimised and help reduce endrin decomposition. The use of non-equilibrium SPME with fast GC could be extended to other groups of environmental contaminants to provide a range of very fast screening methods to keep up with the demands of environmental monitoring.

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