ELSEVIER

Journal of Chromatography A, 964 (2002) 21–33

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination of organochlorine pesticides in ground water using solid-phase microextraction followed by dual-column gas chromatography with electron-capture detection

Bruce A. Tomkins[a,*], Angela R. Barnard[b]

[a]*Environmental Chemistry and Mass Spectrometry Group, Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6120, USA*

[b]*Quality Planning and Assessment Group, Environmental Protection and Waste Services Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6120, USA*

Received 31 January 2002; received in revised form 12 April 2002; accepted 6 May 2002

Abstract

A rapid, sensitive, convenient, and highly quality-assured method is presented for the determination of 19 organochlorine pesticides (OCPs) in small samples (10 ml) of ground water. Samples are initially fortified with 2,4,5,6-tetrachloro-*m*-xylene (surrogate) and decachlorobiphenyl (retention time marker), then extracted with a 30-μm thickness polydimethylsiloxane solid-phase microextraction fiber. The analytes collected are thermally desorbed in a heated gas chromatographic inlet, separated using independent fused-silica capillary columns (''primary'' and ''confirmatory''), and detected using electron-capture detection. Two independent statistical procedures were used to evaluate the detection limits, which typically range between 10 and 40 ng l^{-1}, for these analytes. Method performance was also evaluated using two additional protocols employing ''performance evaluation'' samples, in which authentic ground water samples were fortified to ca. 100 ng l^{-1} in each of at least six OCPs. The method satisfies additional strict criteria based on uniformity of fiber performance and minimal degradation of the thermally-sensitive analytes endrin and DDT.

Keywords: Water analysis; Solid-phase microextraction; Pesticides; Organochlorine pesticides

1. Introduction

Organochlorine pesticides (OCPs) are among the most persistent organic pollutants present in aqueous environments. They present a possible risk to aquatic species because of their inherent toxicity and ability to accumulate in living organisms [1]. For that reason, their presence in water is strictly regulated by legislation to concentrations ranging between less than 10 to 100 ng l^{-1} (parts-per-trillion) [2–4].

Historically, the initial extraction of OCPs from aqueous samples [5] is performed batchwise (separatory funnel) [6] or continuously [7] using liquid–liquid extraction (LLE). Large volumes of both aqueous sample (typically, 1 l) and high-purity organic extracting solvent (typically dichloromethane) are required, and most of the latter is ultimately discarded as chemically-hazardous waste. Analytical methods that employ smaller volumes of initial sample and/or extracting solvent would be

*Corresponding author. Tel.: +1-865-574-4874; fax: +1-865-576-7956.

E-mail address: tomkinsba@ornl.gov (B.A. Tomkins).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)00592-7

preferred. Procedures based on solid-phase extraction (SPE) [8] permit the volumes of both the aqueous samples and extracting solvents to be reduced substantially. However, if the aqueous sample contained particle fines, both the small columns or disks employed were subject to ''plugging''. Passing the sample through additional filtration media might or might not reduce the quantity of particulate matter appreciably.

In 1996, Magdic and Pawliszyn [9] described the application of solid-phase microextraction (SPME) fibers to the determination of OCPs in aqueous samples. Briefly, a coated fused-silica fiber is immersed into a small volume of aqueous sample, and the OCPs present are collected on the coating. The analytes are later desorbed thermally from the coating in the injector port of a gas chromatograph and subsequently analyzed. This approach employed only small volumes of aqueous sample (typically a few milliliters) and no organic extraction solvents. Less particulate matter accumulated on an SPME fiber than on an SPE cartridge or disk; hence, ''plugging'' was reduced substantially. This method was evaluated for its ability to extract 12 organophosphorus, organonitrogen, and OCPs in ultra-pure water using a ''round robin'' test involving 11 laboratories in Europe and North America [10]. The results demonstrated that SPME was a valid method for the determination of a very diversified group of semivolatile compounds at trace ($\mu g\ l^{-1}$) concentrations.

The most widely-used SPME coating for OCP analysis is 100-μm thickness polydimethylsiloxane (PDMS) [9,11–16]. The linear range range for 17 OCPs was 10–5000 ng l^{-1}, with typical detection limits ranging between 0.05 and 1 ng l^{-1}, when using this type of extracting fiber [11]. Young et al. [17] compared the extraction efficiency and carryover for 20 OCPs from aqueous samples using fused-silica fibers coated with 20-, 30-, or 100-μm PDMS. They observed comparable percent average spike recoveries for all three coating thicknesses, but markedly less carryover when the 30-μm thickness coating was employed. SPME provides a very general approach for determining OCP in aqueous samples as diverse as ground, surface, river, tap, drinking, and sea waters [18], as well as diluted human body fluids [19].

Partition ratios, which describe the distribution of a given analyte between aqueous media and a specific fiber coating, provide an objective criterion for judging the suitability of a particular fiber for a specific task. Valor et al. [20] recently published such tables for five different polymeric coatings and 52 pesticides (different classes) and polychlorinated biphenyls (PCBs). Partition ratios calculated for PDMS fibers suggest ''modest'' recoveries for most OCPs.

Most current analytical procedures do not address the determination of hexachlorocyclopentadiene (HCCP), a precursor for numerous OCPs, in ground water. This compound has rarely been reported as a contaminant in drinking water [21], but might well be present in ground water samples taken near an existing or abandoned OCP manufacturing facility. HCCP has been extracted from aqueous samples using dichloromethane or hexane, and from acidified urine samples using light petroleum [22]. This behavior suggested that HCCP, like the OCPs themselves, would be amenable to determinations employing SPME.

The analytical method presented herein extracted OCPs and HCCP from 10-ml samples of authentic or ''model'' ground water using 30-μm thickness PDMS fibers. Analytes are collected for 45 min, desorbed in the injection port of a gas chromatograph, and detected using conventional electron-capture detectors. The injector (thermal desorption) temperature is programmed and maintained at its maximum temperature for only a short period of time. Because the injection temperature is not fixed indefinitely at a high temperature, the ''coating bleed'' from SPME fibers remaining in the injector port is reduced substantially, thereby prolonging the lifetime of the coating.

Several additional measures of quality assurance were included in the method described herein [23]. A new test was developed to ensure that a given fiber had not been ''poisoned'' by a previous determination. The analytical columns employed had to exhibit at least 60% valley resolution (baseline resolution preferred) between closely-eluting analytes and minimal degradation of thermally-sensitive endrin and DDT. The identification of a given OCP analyte was initially performed on a ''primary'' analytical column, then ''confirmed'' using a column

with both a different bonded phase and OCP retention time order. Finally, results obtained by the new method had to be demonstrated equivalent to those obtained using existing approved methods with a set of ''performance evaluation'' samples. Such samples would be prepared independently by a third-party laboratory, then submitted to candidate laboratories for analysis. The results obtained by each analytical laboratory could then be compared to the ''known'' or ''true'' values and evaluated statistically.

2. Materials and methods

2.1. Chemicals

Stock solutions of the following compounds were purchased from Supelco (Bellefonte, PA, USA): α-BHC, γ-BHC, and δ-BHC (1000 μg ml^{-1} each in methanol); DDT, endrin, isodrin, HCCP (5000 μg ml^{-1} each in methanol); concentrated stock solutions containing the 20 CLP OCPs in hexane–toluene (1:1) (2000 μg ml^{-1} in each analyte); and pesticide surrogate standard mix containing 200 μg ml^{-1} each of decachlorobiphenyl (DCBP) and 2,4,5,6-tetrachloro-*m*-xylene (TCMX) in acetone. The minimum purity of each analyte or surrogate compound was 96%. Anhydrous sodium sulfate, sodium chloride, and HPLC-grade methanol and water were purchased from J.T. Baker (Phillipsburg, NJ, USA).

2.2. Stock and spiking solutions

Aliquots of the three stocks solutions of BHC isomers were diluted to a final concentration of 100 ng ml^{-1} in each compound with methanol; this solution was used to test the performance of the SPME fibers. Portions of the DDT and endrin stock solutions were diluted to a final concentration of 10 ng ml^{-1} in each compound with methanol; this solution was used to evaluate the gas chromatographic columns for degradation of endrin and DDT. The surrogate stock solution containing DCBP and TCMX was diluted to a final concentration of 50 ng ml^{-1} in each compound (surrogate spiking solution); a portion was added to every aqueous sample analyzed. Aliquots of the CLP OCP mix, HCCP and isodrin stock solutions were diluted to a final concentration of 10 ng ml^{-1} in each compound with methanol; this solution was used as either the ''master calibrating'' or ''master spiking'' solution for preparing calibration or certification samples of OCPs in ground water. Each of these solutions was prepared independently by qualified analysts. All of these stock and spiking solutions were stored at 4±2 °C in precleaned 20-ml screwcap vials (I-CHEM Research, Hayward, CA, USA) and are stable for at least 90 days.

2.3. Ground water samples

American Society for Testing and Materials (ASTM) ''model'' ground water was prepared as follows: 1.64 g sodium chloride and 1.48 g anhydrous sodium sulfate were diluted to exactly 1 l with HPLC-grade water. A 100-ml portion of this stock solution was further diluted to exactly 1 l with HPLC-grade water to form ''model'' ground water. Samples of clean authentic ground water were kindly provided by the Quality Planning and Assessment Group, Environmental Protection and Waste Services Division, Oak Ridge National Laboratory (Oak Ridge, TN, USA).

2.4. ''Performance evaluation'' samples

''Performance evaluation'' samples were prepared and provided by the Quality Planning and Assessment Group, Environmental Protection and Waste Services Division, Oak Ridge National Laboratory. These were samples of clean authentic ground water fortified to known concentrations of a least six OCPs. They are used to check the performance (identification, accuracy, and precision) of a given analytical laboratory for the determination of OCPs, and are designed to mimic authentic contaminated ground water samples that would be found at the customer's work site. Additional discussion about performance evaluation samples is provided below.

2.5. Solid-phase microextraction equipment

SPME fibers designed for manual sampling (100-μm thickness polydimethylsiloxane, part No. 57300-U; 30-μm thickness polydimethylsiloxane, part No.

57308; 85-μm thickness polyacrylate, part No. 57304), the corresponding holder for manual sampling (part No. 57330-U), a sampling stand (part No. 57333-U), and a heat/stir plate (part No. Z262129-1) were all purchased from Supelco. All fibers (at least five per coating type) were conditioned for at least 1 h at 250 °C, according to the manufacturer's instructions. Micro stirrer bars (''fleas''), 10 mm×3 mm, were purchased from VWR (USA).

2.6. Instrumentation

Both Varian 3400 and 3500 gas chromatographs (Varian, Sunnyvale, CA, USA), each equipped with an electron-capture detector and splitless septum programmable injector (SPI), were used. Each injector was equipped with a low dead-volume splitless injection liner (0.75 mm. I.D., part No. 26364, 05, Supelco) and a ''pre-drilled'' Thermogreen septum (part No. 23168, Supelco) specifically designed for SPME. (After an SPME injection was performed, the fiber remained in the injection port to seal the pre-drilled septum). An SPME inlet guide (part No. 57356-U, Supelco) was used to support the manual holder and its fiber during the desorption process. One instrument was equipped with a ''primary'' analytical column, viz., Rtx-CLPesticides, 0.53 mm×30 m, 0.50 μm film thickness (part No. 11140, Restek, Bellefonte, PA, USA), while the other was equipped with a ''confirmatory'' analytical column, viz., Rtx-CLPesticides2, 0.53 mm×30 m, 0.42 μm film thickness (part No. 11340, Restek). These two columns exhibit somewhat different orders of elution for the target analytes, and are therefore appropriate for ''primary'' and ''confirmatory'' identification. The helium (>99.99% purity) carrier gas flow was set to 6 ml min^{-1} (ca. 45 cm s^{-1} linear flow) at an initial oven temperature of 100 °C. The nitrogen (>99.999% purity) make-up gas flow was set to ca. 20 ml min^{-1}. Raw data was collected using the ''in-board'' printer-plotter for each instrument.

2.7. Instrument operating parameters

The detector temperature was maintained at 300 °C. The injector temperature was programmed from 100 °C (hold for 1 min) to 225 °C (hold for 5 min) at 180 °C min^{-1}, then allowed to return to its initial temperature. The column oven temperature was initially programmed from 60 °C to 150 °C at 25 °C min^{-1}; then 3.5 °C min^{-1} to 275 °C (hold for 5 min). The column oven temperature programming time was approximately 45 min.

2.8. Quality assurance checks for fiber performance and thermal degradation of endrin and DDT

A 100-μl aliquot of methanol solution containing 100 ng ml^{-1} in each of the three BHC isomers was added to 10 ml model ground water in a precleaned 20-ml screwcap vial. A micro stirring bar was added to the diluted solution (final concentration 1 ng ml^{-1} in each isomer), which was stirred briskly and immediately sampled for 45 min with an SPME fiber. The analytes so collected were immediately desorbed in the injection port of either gas chromatograph, separated, and detected as noted above. The same solution was used to check the performance of all SPME fibers on any given day.

A 50-μl portion of the methanol solution containing 10 ng ml^{-1} each in endrin and DDT was added to 10 ml model ground water (final concentration 50 ng l^{-1} in each compound), which was then sampled as described above. This test was performed once each day for each gas chromatograph.

2.9. SPME calibration procedure

Aliquots of the ''master calibrating solution'' (5 to 200 μl) and the ''surrogate spiking solution'' (20 μl) were added to 10 ml model ground water in a 20-ml precleaned screwcap vial. A micro stirring bar was added to the diluted solution, which was then stirred briskly (vortex formation must not occur) and immediately sampled for 45 min with an SPME fiber. The analytes so collected were immediately desorbed in the injection port of either gas chromatograph, separated, and detected as noted above. Typically, the calibrations of the ''primary'' and ''confirmatory'' analytical instruments were performed in tandem.

2.10. Analysis of authentic ground water, certification, or performance evaluation samples

A 20-μl aliquot of the ''surrogate spiking solution'' was added to authentic ground water and performance evaluation samples Aliquots of the ''master spiking'' solution (5 to 200 μl) and ''surrogate spiking solution'' (20 μl) were added to 10 ml model ground water in a 20-ml precleaned screwcap vial. The resulting solutions were sampled and analyzed as described in Section 2.9. Typically, five SPME fibers of the same type were employed for this work. Two each were assigned to the ''primary'' or ''confirmatory'' instrument. The remainder was arbitrarily designated as the ''spare'', was carefully put aside, and was normally not used unless one of the other fibers was broken or was deemed unusable according to the SPME fiber uniform performance test (described below).

2.11. Calculations

The measured integrated peak area data from the electron capture detector obtained for a given analyte spanning the range 0–200 ng OCP l^{-1} were fit to a calibration curve of the form $A=a^2C+bC+c$, where A is the analyte peak area and C is its concentration. The terms a, b, and c, are constants determined by the regression analysis; none were set equal to zero.

3. Results and discussion

3.1. Analytical method optimization

Several independent investigators described the optimization of the sampling conditions for OCPs in aqueous samples. Their collective experiences, rather than additional experimental work, were employed in the present work. Not all of the OCPs evaluated in this study achieve true equilibrium with a given extraction fiber in a reasonable period of time [9–11,13,15–17]. The present work employed a compromise sampling time of 45±2 min. This sampling time also permitted thermal desorptions in the gas chromatograph to begin shortly after the initial sampling was completed, with minimal lag time. The benefits of ''salting out'' such a wide variety of OCPs appears to be mixed at best, improving the recoveries of some analytes while reducing that of others. Therefore, the present method does not add more salt than present in either ''model'' or authentic ground water samples [9,11,14,16,17]. Attempts to improve the recovery of OCPs by adjusting the pH over a range of 2 to 11 [9,11] were generally unsuccessful, although such treatment has been beneficial for other analytes.

Thermal desorption of the OCPs from the fiber coatings are frequently performed for 5 to 20 min at temperatures ranging between 210 and 300 °C [9–11,14–17]. Lower desorption temperatures offer the following advantages: (a) reduction of coating bleed; (b) extension of SPME fiber lifetime; and (c) reduction of thermal decomposition of labile species such as endrin and DDT. In the present work, the temperature of the SPI was programmed rapidly to 225 °C, held for 5 min, then allowed to return to its initial value of 100 °C.

Partition ratio data presented in Valor et al. [20] clearly demonstrated that several commercially-available SPME fibers would be applicable to the current work. In our experience, fibers employing a polydimethylsiloxane–divinylbenzene coating exhibited the greatest number of background peaks; those coated with PDMS (100- or 30-μm film thicknesses) exhibited the fewest; and those employing a polyacrylate coating were intermediate. HCCP was readily-extracted using either 100- or 30-μm thickness PDMS fibers, but not using polyacrylate fibers. These two PDMS fibers both performed well; however, according to Young et al. [17], the 30-μm coating exhibited less carryover and analytes could be desorbed completely at lower temperatures than the 100-μm coating. For all of those reasons, all data reported in this work employed the 30-μm PDMS SPME fibers.

3.2. Routine measures of quality assurance

Four independent criteria were employed to ensure that qualitative and quantitative data generated using the SPME method were correct. These were: (a) uniform performance of the SPME fibers used; (b) minimal degradation of thermally-sensitive analytes such as endrin and DDT; (c) sufficient resolution between closely-eluting chromatographic peaks to

ensure proper integration and reliable quantitation of the analytes involved; and (d) adequate recovery of analytes, as evidenced by surrogate recovery.

Uniform performance of the SPME fibers was a clear concern because it was not possible to determine whether a fiber was no longer extracting properly with a simple visual inspection, unless the fiber had actually been broken and shortened or the coating itself was cracked. For that reason, the performance of a fiber was judged by its ability to extract selected OCP analytes at a specified concentration in a manner similar to other fibers of the same type and lot. The extraction of three BHC isomers, viz., α-BHC, δ-BHC, and γ-BHC (lindane) at a concentration of 1 ng ml^{-1} each was selected because equilibrium between the aqueous and fiber phases could be achieved quickly (approximately 20 min, according to the open literature) and because each analyte was recovered at approximately 1% from a given test solution. The latter implied that the same solution could be sampled repeatedly without significantly reducing the concentration of the analytes present. Table 1 gives the measured integrated peak areas for these three compounds for five 30-μm thickness PDMS fibers employed during method certification (described below). The relative standard deviation (RSD) of the peak areas is less than 10% for each target compound. A fiber was considered unusable when the integrated peak area of all three analytes was less than 80% of the mean value of other fibers of a similar type evaluated on the same day using the same test solution. When reasonably clean ground water samples are extracted using appropriate care and caution, a single fiber should last for at least 100 sample extraction/thermal desorption cycles.

Table 1
Example of SPME fiber evaluation using three BHC isomers[a]

Fiber number	Measured integrated peak area		
	α-BHC	γ-BHC	δ-BHC
1	10 619 512	7 584 329	4 334 153
2	11 829 630	8 911 988	4 729 904
3	11 670 300	8 945 855	4 700 882
4	11 230 876	8 850 908	5 519 532
5	10 924 765	8 779 175	5 156 617
Average	11 255 017	8 614 451	4 888 218
Standard deviation	504 023	579 343	457 641
RSD (%)	4	7	9

[a] Test concentration is 1 ng ml^{-1} each in model ground water.

The extent of thermal degradation of the OCP analytes was evaluated by analyzing a solution containing only endrin and DDT using both ''primary'' and ''confirmatory'' instruments. The instrument was considered suitable for use if the degradation for DDT (as evidenced by the presence of DDE and DDD) and endrin (as evidenced by the presence of endrin ketone) was not greater than 20% each, and not greater than 30% combined [23]. In the present work, the degradation of each target compound was less than 5% on either instrument, thereby indicating that both had satisfied the test for thermal degradation.

Each column needed to satisfy a ''resolution check'' to ensure adequate resolution on its instrument. Typically, a calibration chromatogram obtained from a ''mid-range'' standard (normally 50 or 100 ng l^{-1}) was examined visually to verify that the resolution between two adjacent peaks for target analytes was greater than or equal to 60% [23]. This was accomplished using the following formula: percent resolution$=(V/H)\cdot 100\%$, where V is the depth of the valley between the two peaks and H is the height of the shorter peak. In this work, the resolution between all 24 compounds evaluated using the ''primary'' analytical column was greater than 60%; most of the analytes were baseline-resolved. The same figures of merit were noted for the ''confirmatory'' analytical column for all compounds except for DDD and endosulfan II, which were usually resolved by less than 0.1 min and which did not satisfy the usual criterion for resolution. The ''confirmatory'' analytical column was deemed acceptable for use in the current work because, historically, DDD, but not endosulfan II, had been found in the ground water samples on the specific worksite in question. Furthermore, this was the only analyte pair where such resolution difficulties were observed.

Finally, a ''mid-range calibration check'' sample, consisting of a 10-ml aliquot of model ground water fortified to 50 ng l^{-1} in each of the target OCP compounds, was analyzed at or near the end of each lot of samples. The purpose of this additional measure of quality was to ensure that the detector responses and calibration data did not drift substan-

tially during the course of the analyses performed. The usual acceptance criterion is that the concentrations calculated from the ''mid-range calibration check'' should be within ±10% of the expected value.

Both TCMX and DCBP were evaluated as surrogate compounds for the OCP. In practice, the recovery of DCBP was too erratic for use as a reliable surrogate compound. However, it was included because, as the latest-eluting component in each sample, it could be used as a relative retention time marker and would be essential for identifying some of the later-eluting OCP analytes. By contrast, the recovery of TCMX, which elutes earlier than any of the OCP except HCCP, was reasonably consistent and could be used as a reliable surrogate compound. The initial criterion for the recovery of TCMX surrogate was a minimum 70% when this compound was added to an aqueous sample at 100 ng l^{-1}.

3.3. Sample stability and storage

The US Army Rocky Mountain Arsenal Chemical Quality Assurance Plan [23] recommends that aqueous samples intended for pesticide and PCB determinations be stored at 4±2 °C, extracted within 7 days of receipt, and analyzed within 40 days of receipt. SPME permits the OCPs from an extracted sample to be available for final gas chromatographic analysis not more than 1 h after extraction begins. The key requirement is that the OCP concentrations in ground water samples remain stable during the initial 7-day ''holding time'' period.

Twelve 10-ml aliquots of model ground water were fortified to 50 ng l^{-1} in each of the target OCP and 100 ng l^{-1} of the two surrogate compounds. Six independently-selected portions were sampled using 30-μm thickness PDMS fibers and analyzed when (a) all vials were freshly-prepared and (b) after the vials had been stored in a refrigerator under the recommended conditions for 6 days. One-way analysis of variance was performed for eight OCPs [α-BHC, γ-BHC (lindane), γ-chlordane, heptachlor epoxide, dieldrin, endrin, DDT, aldrin] measured on the 2 quantitation days. A statistically-significant decrease ($P<0.05$) was not observed in the calculated analyte concentrations.

These results suggest that fortified ground water samples extracted using the PDMS fibers would permit consistent OCP quantitations over the usual seven-day storage period. These conclusions generally agree with those reported by Shirey and Mindrup [24] for 100-μm thickness PDMS fibers applied to the extraction of OCPs from aqueous samples.

3.4. Method evaluation and determination of the method reporting limits

The performance of the proposed method was evaluated using two statistical protocols, viz., those of the US Army Rocky Mountain Arsenal [23] and the US Environmental Protection Agency (EPA) [25] to determine the ''method reporting limit'' (MRL) and the ''method detection limit'' (MDL), respectively. The former is equivalent to determining a ''found'' concentration so that both the false positive and the false negative errors are both 5%, as discussed in Hubaux and Vos [26] and Grant et al. [27]. By contrast, the latter is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero [25].

The MRL was evaluated using a procedure established by the US Army [23] and discussed in detail elsewhere [28]. Briefly, 10-ml portions of ''model'' ground water are fortified with the target OCP to concentrations ranging between 5 and 200 ng l^{-1}, representing 0.5 to 20 times a ''target reporting limit'' (TRL) of 10 ng l^{-1}. For this initial certification, the concentrations of the two candidate surrogate compounds, TCMX and DCBP, were constant (100 ng l^{-1}) for both certification and calibration samples. Samples are spiked, extracted, and analyzed as described above, and the resulting OCP concentrations calculated using calibration data obtained on each of two method certification days. The MRL values were calculated using these concentration data and the current software recommended by the Program Manager Rocky Mountain Arsenal for each target OCP [29].

This procedure was performed for both the ''primary'' (Rtx-CLPesticides) and the ''confirmatory'' (Rtx-CLPesticides2) columns. As examples, the spiked (''true'') and analyzed (''found'') concentrations for two representative OCPs, dieldrin and endrin, on both certification days using the primary

Table 2
Comparison of ''found'' versus ''true'' concentrations of dieldrin and endrin obtained using SPME and the ''primary'' analytical column in method reporting limit (MRL) certification samples

''True'' concentration (ng l^{-1})	''Found'' dieldrin (ng l^{-1})		''Found'' endrin (ng l^{-1})	
	Day 1	Day 2	Day 1	Day 2
0	9	8	8	5
5	10	10	9	6
10	12	11	11	9
20	15	15	15	15
50	51	37	44	60
100	110	82	79	101
MRL (ng l^{-1})	35		25	
Estimated recovery (%)	90		88	

analytical column are presented in Table 2. The slope of the calculated linear regression line representing the relationship between the ''found'' and ''true'' values may be taken as a measure of analyte recovery. (A value of 1.00 implies 100% recovery). The average value for the analyte recovery based on all 19 analytes was 0.91 ± 0.11 (mean $\pm$ standard deviation) using the ''primary'' column and 1.09 ± 0.11 (same convention) using the ''confirmatory'' column, as expected when sample preparation is very minimal. A summary of all MRL values obtained using both the ''primary'' and ''confirmatory'' analytical columns is presented in Table 3. The MRL values range between 11 and 47 ng l^{-1}.

Calibration curves usually achieved a plateau at or near the highest test concentration of 200 ng l^{-1}. Reliable concentration measurements could not be calculated at or near this value. For this reason, the tested concentration range employed in the method was ultimately truncated to 5 to 100 ng l^{-1} per OCP analyte in model ground water, even though samples fortified to 200 ng l^{-1} had been prepared, sampled, and analyzed. This observation may be explained in one of four ways: first, the fiber coating volume, which is only 130 nl, may have become saturated with OCPs at or below 200 ng l^{-1}, and it was not possible to collect additional material on the fiber. Second, the electron-capture detector may have become saturated with halogen-containing analytes, particularly for well-recovered OCPs such as heptachlor and heptachlor epoxide. Third, the integration system may not have been able to integrate the large analyte peaks reliably. An adjustment of the integration time constant, for example, may have been necessary to do this properly. Fourth, it was tacitly assumed that the addition of 200 μl of methanol spike to a 10 ml aqueous sample would not affect the partition ratio for the OCPs adversely. Rendering an aqueous sample 2% (v/v) in methanol may have been improper. The preferred practice might be to reduce the maximum concentration of organic solvent present to 0.2% (v/v) methanol, representing a 20 μl methanol spike. As temporary measures, future method certifications should employ either a maximum concentration value of not greater than 150 ng l^{-1} (15 times the TRL stated) or smaller volumes (not to exceed 20 μl) of a more concentrated spiking solution.

3.5. Method evaluation and determination of the method detection limits

MDL values were calculated for all analytes using both analytical columns, as described in Ref. [25]. Briefly, two sets of nine 10-ml model ground water samples (seven required) were independently fortified to 50 ng l^{-1}, then processed as described above. The sample standard deviation of the calculated concentrations for each analyte was usually multiplied by 2.896, which is the one-tailed ''Student's *t*'' value corresponding to eight degrees of freedom (df) and 99% confidence to obtain the MDL. (Occasionally, the sample standard deviation was based on seven values. In such cases, the sample standard deviation was multiplied by 3.143, which is the one-tailed ''Student's *t* table value corresponding

Table 3
Summary of the calculated method report limit (MRL) and method detection limit (MDL) data for OCP extracted from ground water using SPME

Analyte	Primary column Rtx-CLPesticides		Confirmatory column Rtx-CLPesticides2	
	MRL (ng l^{-1})	MDL (ng l^{-1})	MRL (ng l^{-1})	MDL (ng l^{-1})
Aldrin	30	12	37	18
p,p′-DDD	24	19	Not calculated[a]	[a]
p,p′-DDE	17	12	18	38
p,p′-DDT	26	11	36	27
Dieldrin	35	29	15	36
Endosulfan I	26	26	26	37
Endosulfan II	36	33	Not calculated[a]	[a]
Endosulfan sulfate	11	17	34	28
Endrin	25	27	25	42
Endrin ketone	16	14	15	17
Heptachlor	24	16	28	16
Heptachlor epoxide	25	22	16	32
HCCP	36	55	[b]	14
Isodrin	34	13	38	18
Methoxychlor	29	33	36	38
α-BHC	44	24	22	22
α-chlordane	19	13	15	31
γ-BHC (lindane)	28	14	47	31
γ-chlordane	21	13	12	22

[a] DDD and endosulfan II were incompletely resolved at 60% valley, as required in Ref. [23]. Calculations for the MRL and MDL using the confirmation column were not attempted.

[b] HCCP co-eluted with a contaminant on day 2 at 50, 100, and 200 ng l^{-1}, producing a high-bias of at least 50%. No MRL calculations attempted.

to 6 df and 99% confidence). Sample calculations for five representative OCPs using concentration data obtained with the ''confirmatory'' analytical column are presented in Table 4. A summary of all MDL values obtained using both analytical columns is also presented in Table 3. Overall, the MRL values

Table 4
Determination of the method detection limit (MDL) for five representative OCPs using the ''confirmatory'' analytical column

Sample number	Measured concentrations (ng l^{-1})				
	α-Chlordane	*p,p′*-DDE	Heptachlor	Aldrin	Isodrin
1	22	23	26	22	28
2	23	26	29	23	33
3	32	28	31	31	36
4	38	33	33	34	38
5	40	34	34	35	40
6	41	36	38	35	42
7	44	49	38	37	45
8	45	57	40	38	45
9	56	57	43	39	47
Experimental SD	11	13	5.5	6.2	6.2
Student's *t* table value	2.896[a]	2.896	2.896	2.896	2.896
MDL (ng l^{-1})	31	38	16	18	18

[a] One-tailed, 99% confidence, df=8.

ranged between 11 to 44 and 15 to 47 ng l^{-1} using the ''primary'' and ''confirmatory'' analytical columns, respectively. Using the same convention, the MDL values ranged from 11 to 55 and 14 to 42 ng l^{-1}, respectively, using the two columns.

3.6. Evaluation of performance evaluation samples

An independent approach for assessing the overall performance of the new method and adding a further level of quality assurance is the routine and periodic determination of OCPs in ''performance evaluation'' (PE) samples [30]. These are samples of ground water that have been fortified with the analytes in question (here, OCPs) to known and predetermined concentrations by an independent (third party) laboratory under a strictly-observed and generally-accepted protocol. Such samples may contain any or all of the analytes in question; however, in general, the suite of analytes selected is representative of those that may be found at a particular worksite. The concentrations of the target compounds are chosen to be at or above the detection limits claimed by a candidate analytical laboratory. PE samples are sent to candidate analytical laboratories under approved storage conditions (here, 4 ± 2 °C) within the normal approved ''holding time'' (here, 7 days) from the time that such a sample is prepared to the time that it must be extracted. Depending upon the quality assurance protocol selected, the PE samples may be submitted as ''single-blind'' (i.e., the candidate laboratory knows that this is a PE sample, but does not know the identity or concentration of the analytes present), or as ''double-blind'' (i.e., the candidate laboratory does not know that the sample in question is a PE sample and does not know either identity or concentration of the analytes present). Overall, PE samples are prepared in such a way that they closely mimic authentic contaminated ground water samples that have been submitted for analysis in the usual manner; however, they have been fortified to known concentrations with analytes known or suspected to be present at a given worksite.

In this work, PE samples were prepared and analyzed under the ''single-blind'' protocol in order to provide the investigators immediate information concerning the suitability and reliability, or the lack thereof, of the candidate analytical procedure. All samples were analyzed as described above, using both ''primary'' and ''confirmatory'' analytical columns. The results were ultimately summarized and evaluated by a collaborating third-party laboratory. The results presented in Table 5, summarizing analytical data collected from three PE samples, clearly demonstrate that the candidate analytical method discussed herein was capable of providing

Table 5
Comparison of ''target'' and ''found'' concentrations of OCPs in three performance evaluation samples

Analyte	PE-1		PE-2		PE-3	
	Target, (ng l^{-1})	Found, (ng l^{-1})	Target, (ng l^{-1})	Found, (ng l^{-1})	Target, (ng l^{-1})	Found, (ng l^{-1})
Aldrin	101	104	94	109	100	123
p,p′-DDE	68	76	105	102	100	103
p,p′-DDT	135	117	94	111	100	77
Dieldrin	135	116	105	110	100	105
Endrin	203	161	141	134	100	134
α-Chlordane	68	71				
γ-Chlordane	101	99				
Isodrin			105	162		
α-BHC					100	116
β-BHC					100	Not detected
DDD					100	112
Heptachlor					100	118
Heptachlor epoxide					100	113
Lindane (γ-BHC)					100	112
Methoxychlor					100	101

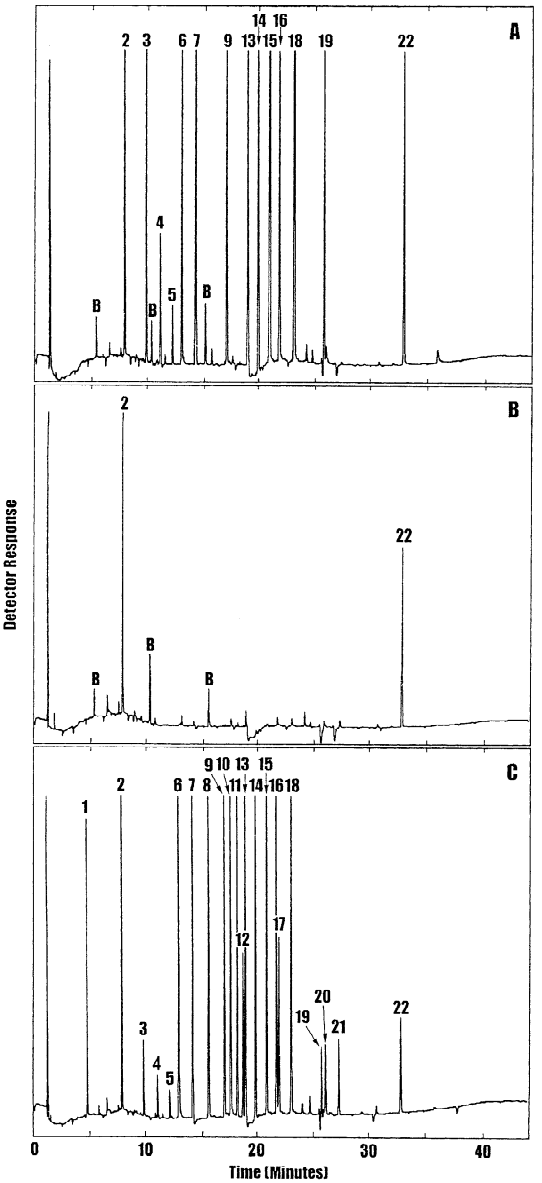

Fig. 1. Comparison of samples analyzed for OCPs using SPME and the ''primary'' analytical column, as described in the text. (A) Performance evaluation sample fortified to 100 ng l^{-1} in each analyte in clean ground water; (B) clean ground water blank; (C) standard containing 50 ng l^{-1} in each analyte in model ground water. Legend: 1=HCCP; 2=TCMX (surrogate); 3=α-BHC; 4=γ-BHC (lindane); 5=δ-BHC; 6=heptachlor; 7=aldrin; 8=isodrin; 9=heptachlor epoxide; 10=γ-chlordane; 11=α-chlordane; 12=endosulfan I; 13=DDE; 14=dieldrin; 15=endrin; 16=DDD; 17=endosulfan II; 18=DDT; 19=methoxychlor; 20=endosulfan sulfate; 21=endrin ketone; 22=DCBP (surrogate). Peaks labeled ''B'' arise from the authentic ground water blank. All samples contain both TCMX and DCBP at 100 ng l^{-1} each.

reliable identification and concentration data at concentrations approximately four times either the calculated MDL or MRL. The inability to detect β-BHC in one of the PE samples was not considered a serious flaw because this compound partitioned poorly into 30-μm thickness PDMS fibers. β-BHC was not recovered from aqueous samples, and it was not declared an analyte in the candidate method. Fig. 1 shows the ''primary'' analytical column chromatograms obtained from a PE sample that had been fortified to approximately 100 ng l^{-1} each analyte in clean ground water, a clean ground water blank, and a standard containing 50 ng l^{-1} in each analyte in model ground water.

An additional protocol that may be employed using the PE samples is ''split sampling'' or ''round robin'', whereby a single batch of fortified ground water is divided into equal portions and sent to independent laboratories for analysis. An independent third-party may then compare the data from each participant against both the ''true'' values and those obtained by other analytical laboratories. The SPME-based procedure, described herein, was one of four participants in such a split-sampling event. Rather than using the full and customary 1-l portion of performance evaluation sample, the SPME-based method was able to generate reliable data using approximately 40 ml of sample, which was submitted in a ''volatile organics analysis'' vial equipped with a PTFE-lined closure. The resulting data, which are summarized in Table 6, show that the results obtained using the SPME-based procedure described in this work compared favorably not only with the known target concentrations but also with concentration data obtained by three independent analytical laboratories using US EPA procedures.

4. Conclusions

SPME is an effective and solventless procedure for extracting OCPs that are present in ground water at concentrations as low as 5 ng l^{-1} (parts-per-trillion). Two independent statistical certification protocols employing both ''primary'' and ''confirmatory'' analyte identification established detection limits for nineteen priority OCPs between 11 and 47 ng l^{-1}. The certification range of the method is

Table 6
Summary of concentration data obtained from a ''split sampling'' event involving a single performance evaluation sample

Compound	Analyte concentrations (ng l^{-1})				
	Target	Lab. 1	Lab. 2	Lab. 3	ORNL
Aldrin	94	91	132	70	108
p,p′-DDE	105	94	110	80	106
p,p′-DDT	94	94	89	70	62
Dieldrin	105	91	115	80	107
Endrin	141	156	134	140	94
Isodrin	165	191	208	130	165

The ORNL method employs SPME.

5–100 ng l^{-1} for these analytes. The applicability and reliability of the candidate method was evaluated using ''performance evaluation'' samples under two different protocols. Taken together, these results demonstrated that the SPME-based method produced data that was equivalent to those generated using more conventional procedures by independent laboratories. The procedure exhibits several advantages over the more traditional procedures based on liquid–liquid extraction, including the use of smaller volumes of aqueous samples, minimal sampling handling, and an absence of expensive, high-purity organic extracting solvents that would be regarded and handled as chemically-hazardous waste after the analysis. A single operator may process approximately ten ground water samples with confirmation in a typical 8-h working day.

The method evaluation and certification also suggested both limitations and possibilities for expanded capabilities. For example, the procedure as described would be applicable to ''clean'' ground water, drinking water, and some forms of surface waters, but not to waste waters and surface waters with a high organic content. Furthermore, some of the samples analyzed during method certification appeared to exhibit concentrations of OCPs that were considerably greater than those expected. It is possible that the injection temperature in this work was, indeed, sufficient to thermally desorb OCPs present at low concentrations ($<$50 ng l^{-1}) from an SPME fiber quantitatively, as discussed in this work, but was incapable of doing so for higher concentrations ($>$100 ng l^{-1}). This condition should be addressed by increasing the thermal desorption temperature slightly, possibly to 250 °C, and by accepting a probable but manageable increase in the potential thermal degradation of labile analytes such as endrin and DDT.

A potentially serious limitation in the procedure as described is the use of only manual SPME to both sample ground water and to perform the gas chromatographic analysis. This feature permits a very simple holder to be used successfully, but also introduces the possibility of severe irreproducibility as operator fatigue becomes apparent or several independent operators with slightly different injection techniques are employed. The overall sample throughput can be improved at least threefold by employing an automated SPME sampler such as the CTC Combi-Pal [Laboratory Environmental Analytical and Pharmaceutical (LEAP) Technologies, Carrboro, NC, USA] [31–33]. Reducing the SPME sampling time is a possible, but less favorable, option because many of the higher-molecular-mass OCPs would not be sampled under equilibrium or near-equilibrium conditions, thereby resulting in a serious loss of sensitivity.

Acknowledgements

The authors thank Mrs. Teresa J. Cochran (Oak Ridge National Laboratory, Environmental Protection and Waste Services Division) for preparing the performance evaluation samples described in this work and for compiling and analyzing the resulting analytical data. Dr. Robert E. Shirey (Supelco) is thanked for providing technical information and material assistance concerning the criteria and testing for SPME fiber uniformity and 30-μm thickness PDMS fibers for this work. This research was sponsored by the US Army Rocky Mountain Arsen-

al, DOE No. 1989-H077-A1, US Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC. The submitted manuscript has been authored by a contractor of the US Government under contract DE-AC05-00OR22725. Accordingly, the US Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

References

[1] A. Turnbull, Chlorinated Organic Micropollutants, Vol. 6, Royal Society of Chemistry, 1966.
[2] Commission of the European Communities, EEC Drinking Water Guideline; 80/799/EEC, EEC No. L229/11-29, EEC, Brussels, 30 August 1980.
[3] Program Manager Rocky Mountain Arsenal, Record of Decision for the On-Post Operable Unit, Sections 1–11, Version 2.0, Vol. 1, Rocky Mountain Arsenal, Commerce City, CO, March 1996.
[4] Book of Lists for Regulated Hazardous Substances, Government Institutes, Rockville, MD, 1990, p. 51. Taken from Code of Federal Regulations: Protection of the Environment, Part 264, Title 40, Appendix IX, US GPO, Washington, DC.
[5] Method 8081A, Organochlorine Pesticides by Gas Chromatography, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, US GPO, Office of Solid Waste, US Environmental Protection Agency, Washington, DC, December 1996, Revision 1.
[6] Method 3510C, Separatory Funnel Liquid–Liquid Extraction, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, US GPO, Office of Solid Waste, US Environmental Protection Agency, Washington, DC, December 1996, Revision 3.
[7] Method 3520C, Continuous Liquid–Liquid Extraction, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, US GPO, Office of Solid Waste, US Environmental Protection Agency, Washington, DC, December 1996, Revision 3.
[8] B.A. Tomkins, R. Merriweather, R.A. Jenkins, J. AOAC Int. 75 (1992) 1991.
[9] S. Magdic, J.B. Pawliszyn, J. Chromatogr. A 723 (1996) 111.
[10] T. Górecki, R. Mindrup, J. Pawliszyn, Analyst 121 (1996) 1381.
[11] K.K. Chee, M.K. Wong, H.K. Lee, in: J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, Cambridge, 1999, p. 212.
[12] I. Brás, L. Santos, A. Alves, J. Chromatogr. A 891 (2000) 305.
[13] R.-A. Doong, P-L. Liao, J. Chromatogr. A 918 (2001) 177.
[14] B.-H. Hwang, M-R. Lee, J. Chromatogr. A 898 (2000) 245.
[15] C. Aguilar, S. Peñalver, E. Pocurull, F. Borrull, R.M. Marcé, J. Chromatogr. A 795 (1998) 105.
[16] C. Aguilar, A. Peñalver, E. Pocurull, J. Ferré, F. Borrull, R.M. Marcé, J. Chromatogr. A 844 (1999) 425.
[17] R. Young, V. Lopez-Avila, W.F. Beckert, J. High Resolut. Chromatogr. 19 (1996) 247.
[18] J. Beltran, F.J. López, F. Hernández, J. Chromatogr. A 885 (2000) 389.
[19] F.J. López, E. Pitarch, S. Egea, J. Beltran, F. Hernández, Anal. Chim. Acta 433 (2001) 217.
[20] I. Valor, M. Pérez, C. Cortado, D. Apraiz, J.C. Moltó, G. Font, J. Sep. Sci. 24 (2001) 39.
[21] F.M. Benoit, D.T. Williams, Bull. Environ. Contam. Toxicol. 27 (1981) 303.
[22] I.R. DeLeon, N.J. Brown, J.P. Cocchiara, S.K. Miles, J.L. Laseter, E.H. Kremer III, L. Makk, J. Anal. Toxicol. 4 (1980) 314.
[23] Rocky Mountain Arsenal, Chemical Quality Assurance Plan, Version I, 3rd ed., Program Manager Rocky Mountain Arsenal, Commerce City, CO, March 2001.
[24] R.E. Shirey, R.F. Mindrup, Using the SPME Portable Field Sampler to Extract Volatiles and Pesticides from Water and Air, presented at the 1998 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.
[25] Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11, Code of Federal Regulations: Protection of the Environment, Pars 100-149, Title 40, US GPO, Washington, DC, revised 1 July 1990.
[26] A. Hubaux, G. Vos, Anal. Chem. 42 (1970) 849.
[27] C.L. Grant, A.D. Hewitt, T.F. Jenkins, Am. Lab. 23 (1991) 15.
[28] B.A. Tomkins, W.H. Griest, C.E. Higgins, Anal. Chem. 67 (1995) 4387.
[29] The Rocky Mountain Arsenal Method Reporting Limit Program, Version 1.0.0 Users Guide.
[30] J. Bates, Standard Operating Procedure for Analytical Laboratory Performance Evaluation System, Revision 1, Standard Operating Procedure Number 2012, Program Manager Rocky Mountain Arsenal, Commerce City, CO, 9 March 2001.
[31] CTC Combi Pal GC Sampler for Headspace and Liquid Injections, http://www.leaptec.com/prodgc.html≠topic_1.
[32] M. Harkness, Varian, personal communication, 1999.
[33] Z. Penton, Method Development Tips for the Automated SPME System, GC Advantage Note 11, Varian, Walnut Creek, CA.