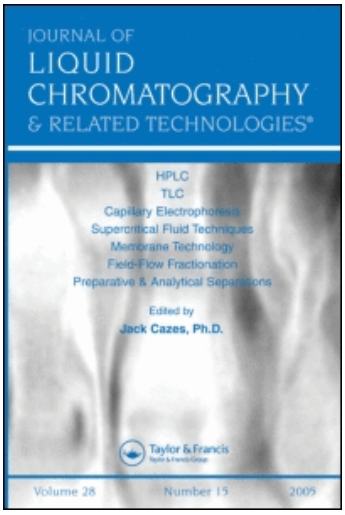

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DETERMINATION OF CHLORDANE IN SOIL BY LC/GC/ECD AND LC/GC/EC NIMS WITH COMPARISON OF ASE, SFE, AND SOXHLET EXTRACTION

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ABSTRACT

Chlordane is a polychlorinated mixture that was used as a long-lived pesticide and now is considered a potential endocrine-disrupting compound. The Environmental Sciences Division is involved in modernizing methods for a number of analytes that are potential target substances for dietary studies, endocrine disrupter studies, Superfund site monitoring, and human exposure studies. In this work, chlordane is determined in soils using each of three different liquid phase/supercritical fluid (CO_2) extractions followed by a two-dimensional chromatographic separation based on high performance gel permeation chromatography (HPGPC) followed by GC/electron capture detection (GC/ECD) and GC/electron capture negative

ion mass spectrometry (GC/EC NIMS). Liquid phase extractions were carried out using accelerated solvent extraction, supercritical fluid extraction, and Soxhlet extraction. The preparative liquid chromatographic part of the work is used in an off-line fractionation mode of HPGPC. Further cleanup is afforded by solid-phase extraction using silica cartridges. Soils spiked at 2 ppm, 0.2 ppm, and 0.02 ppm were quantitated using GC/ECD and GC/EC NIMS with recoveries usually greater than 80%. Soil from a Superfund site and a standard reference material sediment were analyzed as examples of real samples. The modernized methodology developed in this work should offer improved approaches for Superfund analyses and for monitoring methods used in determining potential exposure to endocrine-disrupting compounds while minimizing solvent usage compared to previous methodology.

INTRODUCTION

Among various chlorinated pesticides and industrial chemicals, toxaphene, chlordane, and polychlorinated biphenyls (PCBs) are among the three most common complex polychlorinated mixtures encountered in environmental analysis.[1] The U.S. Environmental Protection Agency, Environmental Sciences Division, maintains a continuous interest in analytical methods for polychlorinated mixtures because of their wide occurrence and persistence in the environment. Our previous efforts to modernize methodology for these three mixtures have centered on toxaphene[2] and PCBs[3] with a brief mention of high temperature GC for polychlorinated terphenyls as well.[4]

Chlordane is a technical mixture of polychlorinated 2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indenes and persists as an environmental contaminant involving both wildlife exposure[5,6] and human exposure,[7,8] and as a suspect endocrine-disrupting compound (EDC).[9] In the past, chlordane found extensive use in termite control because of its persistence and effectiveness. Therefore, contaminated soils and sediments are primary matrices for monitoring potential exposure to this pesticide.

The analytical chemistry of chlordane is extensive with the most commonly used separation/determination based on gas chromatography/electron capture detection (GC/ECD) and GC/electron capture negative ion mass spectrometry (GC/EC NIMS) techniques.[10] Some of the earlier work on chlordane pioneered these approaches.[11-13] The use of gel

permeation chromatography (GPC) as a cleanup tool and as a standard procedure for environmental methods is well established.[14] The more recent versions involving high performance GPC (HPGPC) have resulted in lower solvent usage and greater selectivity.[15] It is within this context that the combination becomes an LC/GC off-line approach.

Extraction technology has also undergone significant development within the last decade.[16] The introduction of supercritical fluid extraction (SFE),[17] microwave-assisted extraction,[18] and accelerated solvent extraction (ASE)[19] has led to faster extractions with lower volumes of organic solvents consumed compared with Soxhlet extraction reference methods.

In this work, we describe the application of three liquid/supercritical fluid extraction approaches to the analysis of chlordane in soil: accelerated solvent extraction, supercritical fluid extraction (CO_2), and Soxhlet extraction. The multidimensional separation/determination of chlordane involves HPGPC followed by solid-phase extraction (SPE) and GC/ECD and GC/EC NIMS.

EXPERIMENTAL

Chemicals

All organic compounds were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA) unless otherwise specified. Other chemicals were from standard sources of supply, and all were used as received. Chlordane, 99% purity, was obtained from Supelco, Inc. (Bellefonte, PA). Decafluorobiphenyl (DFB), 99% purity, was obtained from Aldrich Chemical Company (Milwaukee, WI). Methylene chloride, acetone, and hexane were obtained from Burdick and Jackson (Muskegon, MI).

Extraction

"Local soil" is a mixture of potting soil, purchased locally, mixed with Nevada soil. Other soils were obtained from Idaho and New England. ASE (Dionex ASE 200, Salt Lake City, UT) is an extraction procedure that uses organic solvents at high temperatures under pressure. The ASE system consists of a stainless steel sample cell with electronically controlled heaters and pumps to maintain programed parameters.

The process consists of the following steps: 1) sample cell loading, 2) solvent introduction and pressurization, 3) sample cell heating under constant pressure, 4) static extraction, 5) transfer of extract to sealed vial with fresh solvent wash of soil, 6) nitrogen purge of cell, and 7) loading of next sample.

A 10-gram soil sample spiked with different levels of chlordane was loaded into the extraction vessel, extracted with a 1:1 mixture of methylene chloride-acetone at either 100°C or 150°C. The final volume of the extraction solvent was approximately 15 mL. After extraction, extracts were concentrated to fall within the normal concentration ranges and exchanged, when necessary, into a solvent compatible with the cleanup or determinative method being used. The 15-mL sample was concentrated down to near dryness and brought up to 1.0 mL with methylene chloride (and acetone when necessary for complete dissolution) for subsequent HPGPC fractionation. The Superfund site soil was provided by Jim Johnson of Region 9. The SRM-1941 reference sediment was obtained from NIST (Beltsville, MD).

SFE was done on model 7680T (Hewlett-Packard, Avondale, CA) with the following extraction conditions: density was 0.75 g/mL; pressure was 305 bar; chamber temperature was 80°C; flow rate was 3.0 mL/minute; equilibration time was 20 min; extraction time was 30 min. Thimble volumes swept were 15.9; extraction fluid was 100% CO_2; nozzle temperature was 60°C; trap temperature was 15°C; and trap packing was C_{18} derivatized silica (ODS). Soxhlet extractions were done in a Soxhlet extraction apparatus using about 150 mL of methylene chloride/acetone (50/50) and an extraction thimble obtained from Aldrich Chemical Co. (Milwaukee, WI).

Liquid Chromatography

Automated HPGPC was used to separate chlordane from other interferences in the soil matrix. The GPC system consisted of a guard column (7.8 mm ID X 5.0 cm) and two tandem columns (22.5-mm ID X 25 cm) packed with Phenogel 10-μm particles of 100 Å pore size (Phenomenex, Torrance, CA), a C6UW injector with 1-mL sample loop (VICI, Houston, TX), UA-5 absorbance detector, 260D syringe pump, and Foxy 200 fraction collector (ISCO, Lincoln, NE). Filtered methylene chloride was pumped through the column at 7 mL/min and fractions (30-s interval/tube) 29 to 32 were collected in 12-mm diameter glass tubes. This fractionation step separates most coextractives from chlordane. The combined fractions were blown down to near dryness with a nitrogen stream, spiked with the internal standard (IS), decafluorobiphenyl with perfluoroterphenyl impurity, [unless SPE cleanup is to be used, and taken up with hexane to 1.0 mL.

Solid-phase Extraction

SPE consisted of 3-mL cartridges of silica (Supelco, Bellefonte, PA, USA) that were pre-rinsed with 6 mL of hexane, 6 mL of hexane:ether (50:50 v:v), and followed by 6 mL of hexane. Samples were applied in about 0.4 mL of hexane and then eluted with 0.5 mL of hexane, followed by 4.0 mL of hexane:ether (95:5, v:v). The total eluent was then concentrated to 1 mL after spiking with IS.

Determination of Chlordane

All GC/ECD analyses were performed with a 5890 Series II (Hewlett Packard, Avondale, CA) using a 30-m SPB5 (Supelco) fused silica capillary column with 0.20 mm ID and 0.20-μm film thickness. Detector temperature was 250°C. Samples were quantitated from a calibration curve of chlordane versus internal standard (IS) from 20 pg/μL to 1 ng/μL chlordane with a linear regression correlation coefficient of 0.98 using chlordane peak areas/IS peak areas versus amount of chlordane/amount of IS.

A TSQ-45 (Finnigan-MAT, Sunnyvale, CA) in the negative ion mode was used for quantitation and confirmation of chlordane. Multiple ion descriptor (MID) scans were constructed for monitoring 14 ions, 13 of which were from chlordane (m/z 304, 306, 338, 340, 372, 374, 376, 408, 410, 412, 442, 444, and 446; m/z 482 corresponding to M^- of perfluoroterphenyl (1% impurity in DFB) was monitored for the IS. The IS was generally spiked into extracts at a level representing 0.8 ng/μL (0.008 ng/μL in the perfluoroterphenyl).

GC/ECD results, when reported based on 10 peaks, are the 10 largest responses from chlordane. This results in about 80% of the chlordane response at the high level, and probably 90% or more at the lower levels as the smaller peaks become undetectable. This discriminates better against the background as discussed later.

RESULTS AND DISCUSSION

The main focus of this work is the application of HPGPC to chlordane analysis in soils and the comparison of two newer extraction technologies, ASE and SFE, with Soxhlet extraction.

The determinative approaches using GC/ECD and GC/EC NIMS have been used before in chlordane analyses. The nature of the determination does affect the comparison and is discussed before the results of the extraction methodologies.

HPGPC Fractionation

Fractionation from the HPGPC setup consisted of peak collection from vials #29-32 or from 14.5 min through 16.5 min. This retention time region is also where toxaphene and PCBs elute. Each of the three complex mixtures elute in a single peak which is convenient for collection of the entire mixture. Previous work from our laboratory[2] discussed the possible separation of PCBs from toxaphene in this region. In the case of chlordane in this work, the wide collection window was used to insure quantitative recovery. Chlordane monitoring does not suffer from the same type of interference that affects toxaphene monitoring in the presence of PCBs and oxygen in the ion source under EC NIMS. As a first approximation in HPGPC, larger molecules (generally higher molecular weight) elute earlier whereas smaller molecules (generally smaller molecular weight) components elute later. As reference points, bis-2-ethylhexylphthalate elutes at 12.3 min and sulfur at 21.0 min.

Our approach differs from that of most existing methods that usually take a very wide collection from bis-2-ethylhexylphthalate to the sulfur peak. Thus, HPGPC in our scheme provides the first separation in multidimensional separations and affords us between 10 and 20 fractions for further separations. This approach, beginning with GPC, has been used by Moore and Jorgenson in a comprehensive three-dimensional scheme.[20] We have previously reported two- and three-dimensional separations in an off-line mode where orthogonal separations offer a general high-resolution approach to any residue analysis problem.[21] In our applications, reverse phase HPLC was followed by capillary zone electrophoresis for the two-dimensional separation and HPGPC preceded these two for a three-dimensional separation with each dimension based on a different separation principle. In the present case, HPGPC is followed by GC for an orthogonal two-dimensional approach that is not comprehensive or directly coupled. When this fractionation is coupled to the highly selective EC NIMS, very specific and sensitive determinations for chlordane are obtained.

Determination Issues

Chlordane presents real problems for the dynamic range of detectors. This results first from the multicomponent nature of the material that contains scores

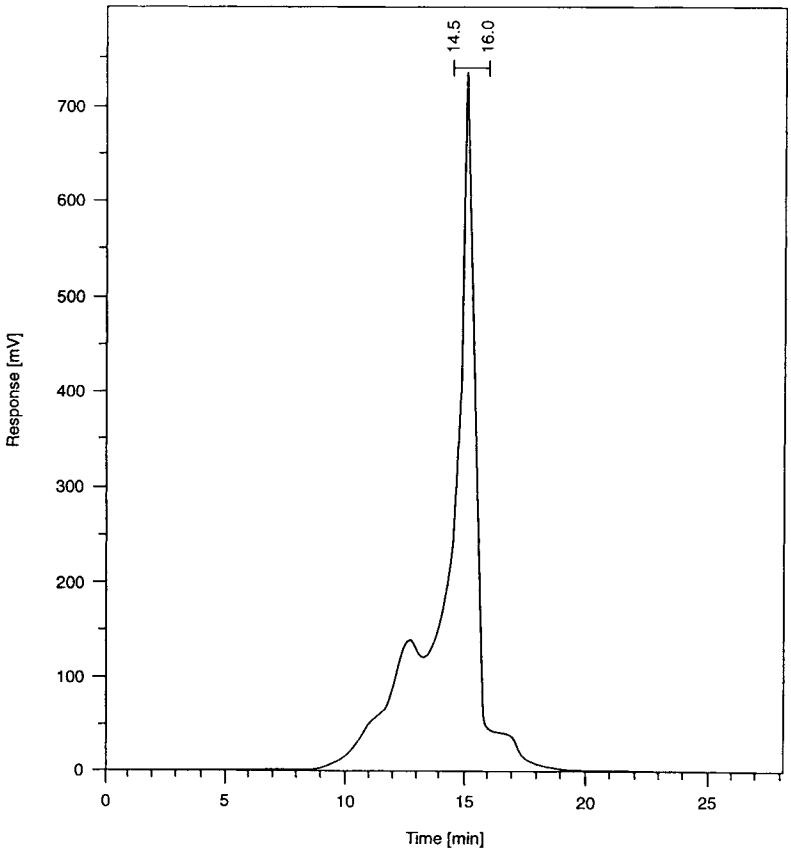

Figure 1. HPGPC/UV response for soil extract using the ASE technique.

of resolvable components that vary from low fractional percentages of the total composition to the 8 to 10 major components readily detectable by GC/ECD and GC/EC NIMS. The second source of variable range of response concerns the residue level in the sample which in our study ranged from 2 ppm to 0.004 ppm . A third variability concerns the dynamic range of the NIMS response itself and the ability to detect relative abundances of ions from 100 % to about 1 %. The interplay of these three factors results in practical calibration ranges of no more than 100. Samples can be either concentrated or diluted to remain within the dynamic range/calibration range. The cleanup step from HPGPC affords a fraction illustrated in Fig. 1. Higher molecular weight extractives elute before chlordane. We retain the option of analyzing other fractions from

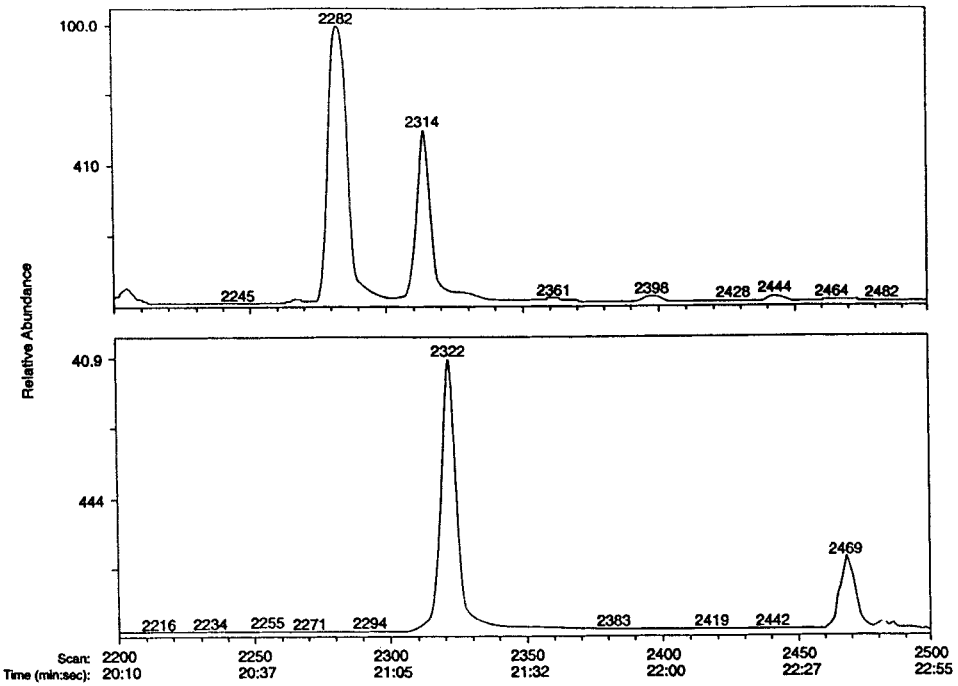

Figure 2. GC/EC NIMS selected ion responses (m/z 410 and 444) for standard of chlordane.

this step or submitting them to further fractionation using other separation techniques such as HPLC. Complex mixtures such as chlordane elute as one peak by HPGPC. A chlordane standard using a 25-m SPB5 column yields about ten major peaks that are easily detected. The chlordane responses span about 5 minutes from retention times of 12 to 17 min.

Figure 2 illustrates responses for m/z 410 and 444 representing octachloro and nonachloro components of chlordane monitored by GC/EC NIMS. We obtained linear regressions of the ratio of the integrated chlordane response/area of the internal standard versus the ratio of chlordane/internal standard amounts for standards from about 20 pg/μL to 1 ng/μL. The combination of HPGPC/GC in an off-line mode provides a powerful two-dimensional approach for environmental analysis. When less specific detection or lower detection limits are sought, further dimensionality can be used based on other liquid separation techniques such as HPLC or capillary electrophoresis.[21]

Table 1

Comparison of GC/ECD and GC/EC NIMS Results for Spiked Soils with ASE at 100°C using 50%/50% v/v Methylene Chloride/Acetone, No SPE Cleanup

Spiked Level ppm	ppm GC/ECD; 10 peaks Only	% Recovery GC/ECD; 10 Peaks Only	Avg ±%SD; Avg ± %SD 10 Peaks Only	ppm GC/EC NIMS	% Recovery GCEC NIMS; Avg ± %SD
2.0	2.380; 1.686	119.0; 84.3		1.89	94.1
2.0	1.576; 1.290	78.8; 64.5		1.64	82.1
2.0	1.744; 1.466	87.2; 73.3	95.0±22; 74.0±13	1.45	82.9; 82.9±13
0.200	(a)	(a)		0.0071 (a)	3.6 (a)
0.200	0.380; 0.124	>100.; 62.0		0.178	88.5
0.200	0.357; 0.184	>100.; 92.0	(a) 77.0±19 (b)	0.155	77.8; 83.1±5.4 (b)
0.020	0.215; 0.036	>100.		0.0174	86.9
0.020	0.312; 0.045	>100.		0.0233	116.
0.020	1.23; 0.030	>100.		0.0170	85.0; 96.0±18
0.020	ND	ND		0.238 (c)	119. (c)
0.020	ND	ND		0.203 (c)	101. (c)
0.020	ND	ND		0.290 (c)	145.; 122±18 (c)

(a) Sample was substantially lost. (b) % difference. (c) Extraction performed at 150°C. ND = not determined.

Recoveries Obtained from ASE Extractions

Table 1 presents recovery data for spiked soils undergoing ASE followed by HPGPC fractionation. The extractions are complete in about 20 minutes and use about 15 mL of solvent. Advantage is taken of the faster kinetics of extraction with solvents heated well above their boiling points but kept liquid by the increased pressure. The recoveries are fairly consistent over the three levels by GC/EC NIMS, and range from about 78% to 116% at extraction temperature of 100°C. The recoveries reflect the combination of extraction, HPGPC, and concentration at each step. A 90% recovery at each step results in $(0.90)^4$ or 66% whereas 99 % at each step results in 96% overall recovery. The concentration step is a source of variability and for large solvent volumes (e.g.,

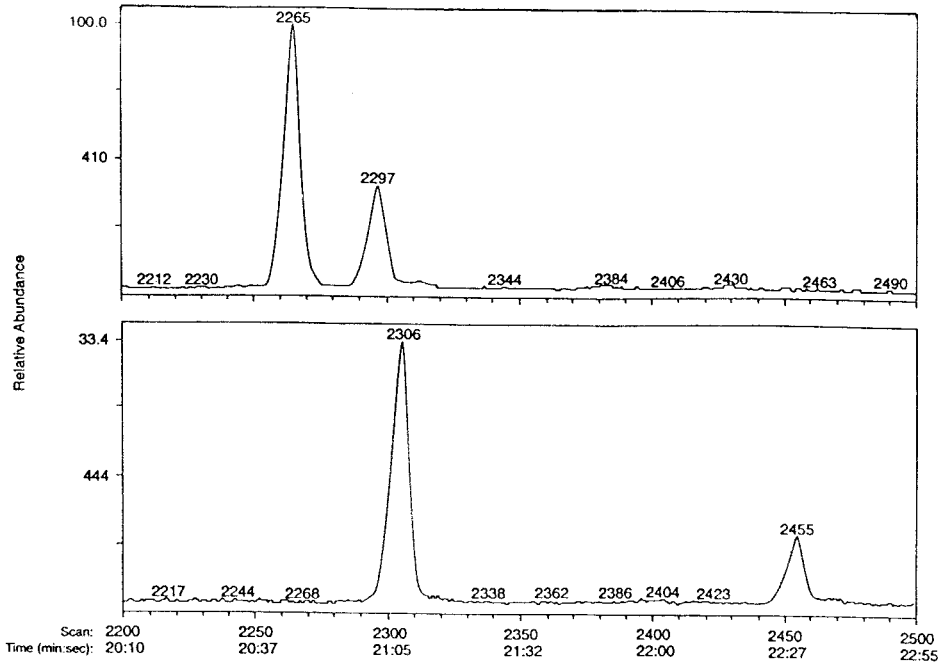

Figure 3. GC/EC NIMS selected ion responses (m/z 410 and 444) for 0.02-ppm level of chlordane in soil.

from Soxhlet extraction) is best provided by a Kuderna-Danish concentration procedure.[1] The last three rows of the table provide recovery data for extractions at 150°C. These data indicate that recoveries may be increased slightly by the higher extraction temperatures.

Fig. 3 provides an example of the responses of m/z 410 and 444 by EC NIMS obtained from an extract of soil spiked at the 0.020 ppm level. The detection of chlordane is specific and consists of a number of ion clusters encompassing Cl_5 to Cl_9 found in retention time windows. Qualitative identification is made on the basis of a comparison between the responses of a standard to those of a sample. For soil samples, extensive weathering of the residue may not significantly alter its composition. For biological samples and sediment samples, changes in the relative amounts of different congeners is likely. The present approach based on the technical chlordane standard does not quantitate on the basis of specific isomers.

The GC/ECD data indicate a positive bias that can be compensated for, in part, by concentrating on the ten most abundant components. At the 0.02 ppm level, GC/ECD is badly compromised by soil coextractives even after HPGPC fractionation. Further cleanup by SPE is discussed in conjunction with Soxhlet extraction.

The ASE technique appears to have performed well as an exhaustive extraction with the solvents chosen. Comparison to SFE and to Soxhlet are discussed below.

Besides time and solvent savings, there is considerable savings in terms of the automated capability of ASE to perform 24 extractions before reloading cells. The extracts are recovered already filtered so that considerable manual manipulations are avoided as for sonication extractions. The vials do need to be disassembled and cleaned before reloading for the next batch of samples. With sufficient numbers of vials, this operation can be performed during the next extraction round. We used concentration by evaporation under nitrogen to prepare the extracts for final separation/determination with Kuderna-Danish concentration for the set of samples extracted at 150°C.

Recoveries from SPE

Table 2 presents recovery data for SPE cartridges of silica as determined by GC/ECD for standards. The recoveries were quantitative and likely presented no major losses of sample. This step serves to eliminate some polar coextractives that might be present and was advantageous for the GC/ECD determinations. For GC/EC NIMS, this is an optional step.

Recoveries from SFE

Table 3 presents a preliminary study of SFE based only on the GC/ECD determination using HPGPC cleanup in combination with this more selective extraction. (Later we shall discuss SFE results in combination with MS in an abbreviated sample-handling approach.) The SFE provided a relatively clean extract that did not require extensive concentration. Chlordane is expected to be relatively easy to extract by SFE with discrimination against more polar components of soil. A disadvantage of SFE could be an efficient extraction of fatty type components including aliphatic hydrocarbons. These are either removed in the HPGPC fractionation step or are transparent to EC NIMS.

Table 2

Recovery of Chlorine After SPE Determined by GC/ECD

Spiked Level ppm	% Recovery GC/ECD; Ave ± %SD
0.200	103
0.200	126
0.200	123; 117 ± 11

Table 3

Recoveries Determined by GC/EC Using Supercritical Fluid Extraction of Soil with HPGPC Fractionation

Spike Level ppm	ppm GC/ECD	% Recovery GC/ECD	ppm GC/ECD 10 Peaks Only	%Recovery ppm GC/ECD 10 Peaks Only
2.0	2.44	122	1.78	88.8
2.0	2.54	127	1.84	92.2
0.200	0.565	283	0.226	113
0.200	0.497	248	0.245	122
0.020	ND	ND	ND	ND
0.020	ND	ND	ND	ND

ND = Not determined because of high background of coextractives.

The extraction fluid consisted of 100% CO_2 combined with an extraction temperature of 80°C. Hawthorne et al. have discussed the overriding importance of temperature with SFE compared with considerations of density and use of modifiers.[22] With spiked samples, recoveries are expected to be higher than with naturally contaminated and weathered samples.

Soxhlet Extractions

Table 4 offers Soxhlet extraction recoveries that may be compared with results of the previous extraction techniques. The recoveries are fairly consistent within a spiking level but differ substantially between levels. We do not have a definitive explanation for the variation. We speculate that the evaporative-concentration step may be the cause of variations because the

Table 4

Comparison of GC/ECD and GC/EC NIMS Results for Spiked Soils Using Soxhlet Extraction for 24 hr with 50%/50% v/v Methylene Chloride/Acetone; SPE Cleanup

Sample Level ppm	ppm GC/ECD	% Recovery GC/ECD; Avg ± %SD	ppm GC/EC NIMS	% Recovery GC/EC NIMS; Avg ± %SD	ppm GC/ECD 10 Peaks Only %Recovery GC/ECD	Avg ± %SD
2.0	1.676	83.8	2.68	134.	1.320; 66.0	
2.0	1.828	91.4	3.24	162.	1.428; 71.4	
2.0	1.372	68.6; 81.3±14	1.56	78.0; 125±34	1.102; 55.1	64.2±13
0.200	0.093	46.7	0.077	38.7	(a)	
0.200	0.165	82.5	0.117	58.4	(a)	
0.200	0.123	61.5; 63.6±28	0.094	46.8; 50.0±21	(a)	
0.020	ND	ND	ND	ND	ND	
0.020	ND	ND	ND	ND	ND	
0.020	ND	ND	ND	ND	ND	

(a) Not determined for this set. ND = Not determined because of high background levels of chlorine in this sample set.

HPGPC and SPE steps are relatively quantitative. In the case of the Soxhlet extract, considerable solvent must be concentrated in contrast to ASE or SFE. The Soxhlet extract was also subjected to SPE whereas the ASE extract was not. There could be added variance in this step as well.

In comparison with Soxhlet extraction, ASE and SFE provide as good or better recoveries. This finding is consistent with the results described by original work with the ASE.[23] Both SFE and ASE provide convenient and automated sample handling. They result in lower solvent usage and more concentrated extracts. The Soxhlet extractions on the other hand can be carried out in parallel and offer an inexpensive approach. Obviously, there is more time involved, but the technique is simple. A limitation is that the temperature of extraction cannot be raised above the boiling point of the solvents used.

SFE with Direct Determination by GC/EC NIMS

Table 5 introduces data concerned with an abbreviated approach for determining chlordane in relatively clean matrices. In this technique, multidimensional separations are avoided by using the extract directly afforded

Table 5

Supercritical Fluid Extraction of Spiked Soils with Direct Determination of Recoveries by GC/EC NIMS

Spike Level ppm	ppm GC/EC NIMS	% Recovery GC/EC NIMS; Avg ± %SD
2.0	2.40	120.
2.0	1.35	67.5
2.0	2.12	106; 97.8±28
0.200	0.195	97.5
0.200	0.209	105; 101.±4.0 (a)
0.200	ND	ND
0.020	0.0272	136
0.020	0.0257	128; 128±6.3
0.020	0.0257	128; 128±6.3

(a) Percent difference. ND = not determined.

by SFE. The selectivity is high for GC/EC NIMS, and this enables a direct determination to be made. It is not expected that this approach would be successful for a complex matrix such as food or highly contaminated soils or similar matrices such as sediments.

ASE Extraction of Real World Samples

Results are reported for EC NIMS determinations of chlordane in a Superfund site soil from Region 9 and for a NIST reference sediment SRM-1941. Both samples were extracted using ASE at 100°C with HPGPC cleanup. We found chlordane at the levels of 3.05 ppb and 24.3 ppb in the soil and SRM-1941 sediment, respectively. Previous work has determined individual components (e.g., α-chlordane, γ-chlordane, heptachlor, and trans-nonachlor) at the 1 to 2 ppb levels.[24,25] Although these results are not directly comparable because we quantitate as the chlordane technical mixture, nevertheless, levels determined are consistent with the independently determined three or four individual components. Both samples had numerous additional components consistent with the presence of chlordane or chlordane-like compounds.

CONCLUSIONS

Comparison among three extraction techniques has resulted in finding similar recoveries of soils spiked with chlordane. Thus, ASE, SFE, and Soxhlet extraction can be used with confidence for this analyte in soils. Our results may be compared with recently reported results evaluating microwave-assisted extraction in comparison to Soxhlet, sonication, and supercritical fluid extraction. Liquid extraction techniques offer a convenient and quantitative method of recovering the analytes. The application of multidimensional separations combining HPGPC and GC in an off-line mode is further illustrated.

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