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Field detection of organochlorine pesticides by thermal desorption gas chromatography–mass spectrometry

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ABSTRACT

Thermal desorption gas chromatography–mass spectrometry (TDGC–MS) was evaluated for field detection of organochlorine pesticides in soil/sediment and water. Rapid, 3 min/sample, TDGC–MS selected ion monitoring (SIM) yielded detection limits of 50 ng/g and 40 ng/l pesticide in soil (2 g) and water (500 ml), respectively, with measurement precision <40%. MS total ion current–selected ion extraction (TIC–SIE) measurements yielded somewhat higher detection limits with measurement precision <20%. Examples of selective pesticide detection in the presence of a wide variety of environmental contaminants in soils, pond and sea waters are provided.

INTRODUCTION

Because of their acute and chronic toxicities as well as resistance to environmental degradation, the detection of organochlorine pesticides and metabolites has received much attention [1–11]. The ability to provide rapid, on-site analyses of complex samples collected from hazardous waste sites as well as livestock and agricultural farms has grown in importance over the last five years. High-resolution capillary gas chromatography (GC) with either mass spectrometry (MS) or electron-capture detection (ECD) provide the most often employed analytical techniques. Although MS can provide positive compound identification, extensive sample preparation procedures are required compared to the more selective ECD for highly contaminated samples. On the other hand, the ECD is especially useful when chlorinated pesticide concentrations are below the GC–MS detection limit. The non-descriptive nature of ECD, however, raises concerns about data reliability [12]. Multi-step sample preparation procedures in addtion to the significant difference in MS and ECD hardware costs presumably account for the 7-fold difference in commercial laboratory analytical costs between GC–MS and GC–ECD analyses.

In this paper, we describe an approach based on thermal desorption (TD) GC sample introduction and selected ion monitoring (SIM) MS detection for 14 organochlorine pesticides and metabolites in soil and water. The research presented is, in part, an on-going effort to provide rapid "field-practical" screening technologies for the analysis of complex hazardous waste site and agricultural samples. Toward that end, TDGC–MS has been developed and "field-validated" for polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in soil/sediment as well as the US Environmental Protection Agency (EPA) listed volatile organic compounds (VOCs) in soil and water [13–16]. For example, 2 min/sample PCB and PAH screening level measurements, with $\leqslant$ 40% measurement precision, have been shown to compare favorably against EPA standardized procedures [14–16]. In contrast, the more quantitative PCB,

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PAH and VOC methods required 10–25 min/analysis and yielded run-to-run relative standard deviations (R.S.D.s) within 30%. The more quantitative TDGC–MS methods provide data comparable to current EPA standardized methods. Results delineating linear dynamic range, minimum detectable amount as well as simple, field-practical pesticide soil–solvent and water–solid-phase extraction procedures are provided. Data will be presented documenting SIM selectivity for pesticide detection in the presence of large quantities of background organics. Rapid, field-practical, TDGS–MS measurements should provide increased data output/unit time and thus, better delineation of hazardous waste site conditions.

EXPERIMENTAL

A thermal desorption gas chromatography–mass spectrometer (Bruker, Billerica, MA, USA) was used in this study. The instrument was powered in the field by 24 V of direct current supply by four 6-V batteries (Trojan J250 Deep Cycle, North Wales, PA, USA). For laboratory MS operation, electrical service was provided through conversion of 110 V a.c. to 24 V d.c. by a VF Series power supply (Deltron). The TDGC–MS instrument consisted of a 3.5-m flexible hose which was attached to the sample inlet system of the mass spectrometer on one end, and on the other a stainless-steel mesh sampling head. The sampling probe head and the hose (GC oven) can be heated from ambient temperature to 260 and 240°C, respectively. Fitted within the hose was a 3.5-m DB-5 capillary column (J&W Scientific). Ambient air served as the carrier gas. Fitted between the sample probe assembly and the mass spectrometer inlet was a methyl silicone membrane which excluded oxygen from entering the electron impact (EI) ionization source. Sample was introduced by placing the heated sampling probe head directly onto the analyte, which was previously injected onto an aluminum foil-covered dish, followed by direct thermal desorption into the GC column. The mass spectrometer was auto-tuned to $H_2O(g)$ (18 amu) and Ar (40 amu) in air *and* a mixture of fluorinated hydrocarbons (FC-77; 69, 100, 119, 169, 219, 269, 331, 397 amu).

In this study, SIM and total ion current–selected ion extraction (TIC–SIE) mass spectrometry were evaluated. Data acquisition was provided by either an on-board microprocessor (SIM) or by a portable computer (TIC–SIE). For confirmatory analyses a HP5890 GC with an electron capture detector, (Hewlett Packard, Avondale, PA, USA) was used. The TDGC–MS and GC–ECD operating conditions are shown in Table I. Detailed description of the TDGC–MS hardware has been reported elsewhere [14,15].

The linear dynamic range was evaluated for the pesticides over a wide concentration range using both the SIM and TIC–SIE-MS detection modes. A 10-μl portion of a standard pesticide mixture (100 ng/μl per pesticide for SIM and 200 ng/μl per pesticide for TIC–SIE) was co-injected with 100 ng of an internal standard ([$^2H_{10}$]phenanthrene) onto an aluminum foil-covered dish. After TDGC–MS analysis, the solution was diluted and each dilution analyzed under the same conditions. This process was continued until signals from these concentrations were no longer observable. In the SIM mode, signal response was the peak height of the selected

TABLE I

EXPERIMENTAL CONDITIONS FOR TDGC–MS AND GC–ECD DETECTION OF THE ORGANOCHLORINE PESTICIDES

TDGC–MS conditions	
GC column	DB-5 (5% phenyl, 95% methyl), 3.5 m × 0.32 I.D., 0.25 μm film
Carrier gas	ambient air, 3.5 ml/min (120°C)
Temperature program	(1) Semi-quantitative: 120 to 240°C at 18°C/min (2) Quantitative: 100 to 180°C at 6°C/min
Sample probe temperature	260°C
Mass range	99–390 amu
Mass scan time	1 s
GC–ECD conditions	
GC column	DB-5, 30 m × 0.25 I.D., 0.25 μm film
Carrier gas	Helium, 1 ml/min (150°C)
ECD make-up gas	5% methane in argon, 30 ml/min
Temperature program	150 to 280°C at 15°C/min, 280°C for 5 min
Injection port temperature	170°C
ECD temperature	325°C

TABLE II

SIM AND TIC–SIE FRAGMENT IONS AND RELATIVE ABUNDANCES (%)

No.	Compound	Ion (relative abundance, %)	
		SIM	TIC
1	α-Benzene hexachloride (BHC)	219 (74,9), 181 (100) 221 (38.8), 263 (0.0)	219, 217, 221
2	β-BHC	(same as α-BHC)	
3	γ-BHC	(same as α-BHC)	
4	δ-BHC	(same as α-BHC)	
5	Heptachlor	100 (100), 274 (51.9) 272 (64,7), 261 (0.0)	100, 274, 272
6	Aldrin	263 (100), 261 (64.7) 101 (100), 293 (41.6)	263, 261, 101 293
7	Heptachlor epoxide	353 (100), 355 (80.5) 351 (51.9), 357 (38.8)	353, 355, 351 351
8	Endosulfan 1	195 (100), 241 (86.5) 207 (74.9), 387 (0.0)	195, 241, 207
9	Dieldrin	108 (100), 263 (20.1) 277 (15.0), 207 (0.0)	108, 263, 277
10	4,4′-DDE	246 (100), 318 (80.5) 316 (60.1), 235 (0.0)	246, 318, 248
11	Endosulfan 2	(same as Endosulfan 1)	
12	4,4′-DDD	235 (100), 237 (64.7) 165 (44.8), 178 (11.2)	235, 237, 165
13	Endosulfan sulfate	272 (100), 274 (92.8) 277 (44.8), 195 (0.0)	272, 274, 277
14	4,4′-DDT	246 (20.1), 235 (100) 237 (69.6), 178 (0.0)	235, 237, 165
15	[$^2H_{10}$]Phenanthrene (internal standard)	188 (100), 187 (21.6) 189 (16.2), 263 (0.0)	188, 187, 189
16	Endrin	317 (55.9), 315 (38.8) 345 (25.0), 343 (18.7)	317, 315, 345
17	Endrin aldehyde	345 (44.8), 347 (25.0) 343 (28.9), 349 (9.7)	345, 347, 343
18	Endrin ketone	317 (51.9), 319 (33.5) 315 (35.9), 321 (11.2)	317, 319, 315

ion current (in logarithmic scale). In the TIC–SIE mode, the selected ion current for each target analyte was manually extracted and integrated from the TIC chromatogram. The identification and quantitation ions and their relative abundances selected for each pesticide are listed in Table II. Response factors (*RF*) were calculated over the linear concentration range; $RF = (A_{std}C_{is})/A_{is}C_{std})$, where A_{std} or A_{is} and C_{std} or C_{is} are TIC–SIE and SIM signals and concentrations for the pesticides or [$^2H_{10}$]phenanthrene, respectively.

Soil samples were prepared as follows: 2 g of soil were placed in a 4 ml sample vial with PTFE-lined screw cap, 2 ml hexane were added and the vial was shaken for 2 min. The extract was then filtered through a disposable 0.45-μm pore size PTFE microfilter (Supelco, Bellefonte, PA, USA) and was analyzed by TDGC–MS without any additional cleanup steps. Two soil types were studied: a poorly to moderately sorted fine to medium sand and a very poorly sorted clay to coarse sand.

For water samples: a 500-ml water sample was drawn by vacuum through a disposable C_{18} Sep-Pak Plus solid-phase extraction (SPE) cartridge (Waters, Milford, MA, USA) at a flow-rate of *ca.* 100 ml/min. The cartridge was dried by drawing

purified air through the cartridge under vacuum for 8–10 min. HPLC-grade hexane was used to elute the pesticides with the analyte collected within the first 1 ml. The extract was analyzed as described above. Three different water samples were used: deionized water, pond water (Mystic Lake, Medford, MA, USA) and sea water (Revere, MA, USA). Pond water and sea water were pre-filtrated by a 0.45-μm nylon 66 membrane before SPE. Field blanks were extracted using the same procedure. SIM and TIC–SIE conditions were used as described above. C_{18} cartridges were used as supplied by the manufacturer.

Evaluation of SIM detection as a selective detector was accomplished by analyzing known quantities of a standard pesticide solution in the presence of either a PCB standard solution or a mixture of Acid–Base–Neutral (A/B/N) standards. The PCB standard contained 1 isomer from 9 of the 10 chlorination levels (Concentration Calibration Standard

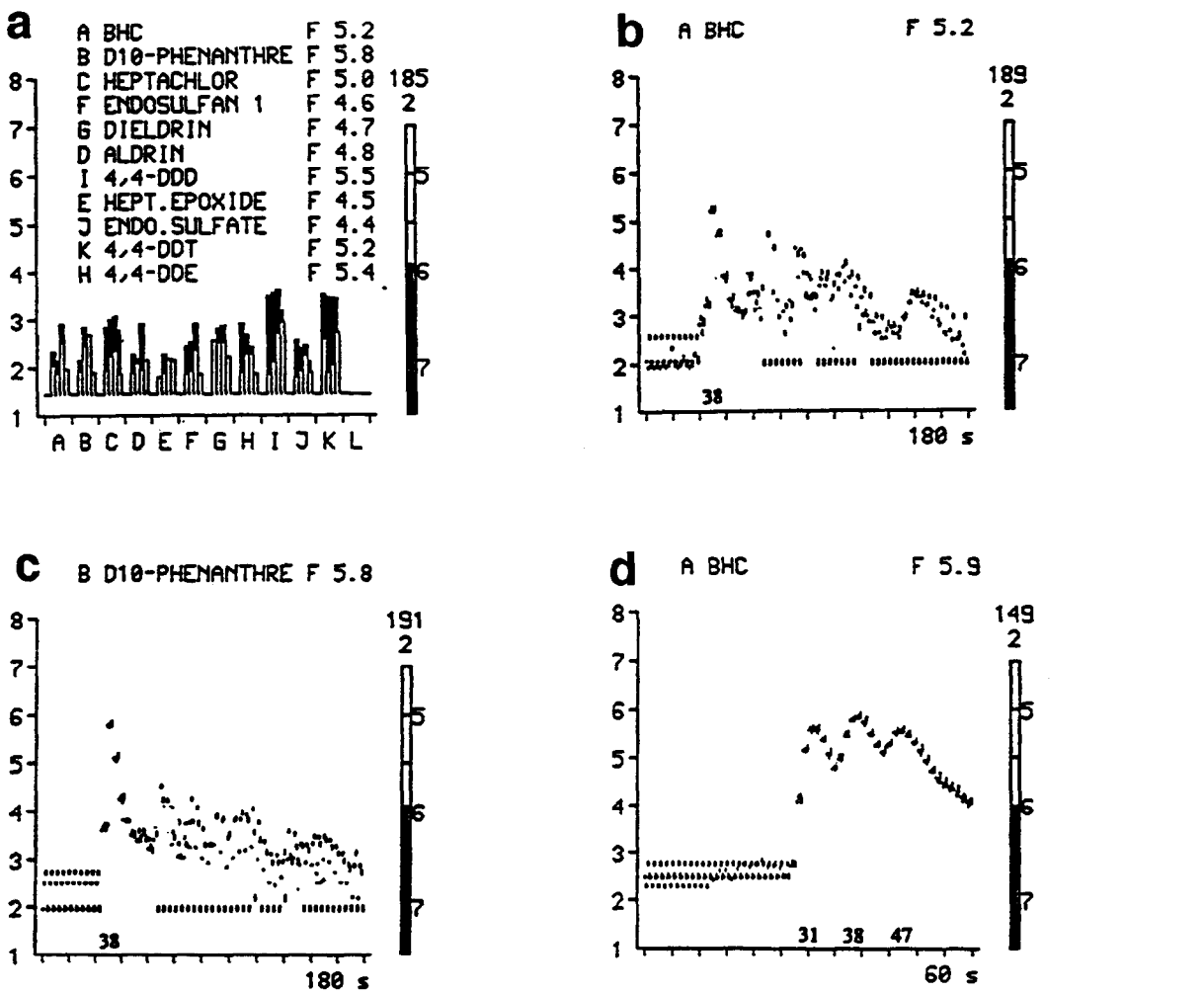

Fig. 1. (a) Typical pesticide (200 ng/compound) and [$^2H_{10}$]phenanthrene (100 ng) SIM signal readout; A = BHC; B = [$^2H_{10}$]phenanthrene; C = heptachlor; D = aldrin; E = heptachlor epoxide; F = endosulfan 1; G = dieldrin; H = 4,4′-DDE; I = 4,4′-DDD; J = endosulfan sulfate; K = 4,4′-DDT. (b–d) Selective ion chromatograms (signal *vs.* time curves) for (b) γ-BHC (retention time: 38 s), (c) [$^2H_{10}$]phenanthrene (retention time 38 s) and (d) BHC isomers (retention times: α-BHC: 31 s; β- and γ-BHC: 38 s; δ-BHC: 47 s). F values represent log values of SIM ion current.

Mixture, Ultra Scientific, North Kingstown, RI, USA). The A/B/N mixture consisted of 63 semivolatile organics and was prepared by mixing 6 commercial standards (Supelpreme-HC Benzidines Mix, Supelpreme-HC Phenols Mix, Supelpreme-HC Polynuclear Aromatic Hydrocarbons Mix, Supelpreme-HC Base-Neutrals Mix 1, Supelpreme-HC Base-Neutrals Mix 2 and Supelpreme-HC Internal standards Mix, Supelco).

Organochlorine pesticides were purchased from Chem Service (West Chester, PA, USA) and the internal standard, [$^2H_{10}$]phenanthrene, from Cambridge Isotope Laboratories (Woburn, MA, USA). A standard pesticide solution was also purchased from Accustandard (New Haven, CT, USA). HPLC-grade methanol and hexane were purchased from Aldrich (Milwaukee, WI, USA) and used as received.

RESULTS AND DISCUSSION

Rapid on-site TDGC–MS analysis has been developed for organochlorine pesticides in soil and water. Results are based on "field-practical" sample preparation procedures, direct TD of analyte from an organic extract *and* SIM (semi-quantitative) or TIC–SIE (quantitative) detection. Figs. 1a and 2a illustrate SIM signal response and the corresponding TIC chromatogram under the same temperature-programmed GC conditions (see Table I, program 1). Table II lists peak numbers, associated compound identities and their relative intensities. For SIM, cells A–K depict signal intensities for the four ions monitored for 10 of the pesticides and the internal standard, [$^2H_{10}$]phenanthrene. The white bars represent the background levels of the four ions selected for detection while the black bars indicate the amount of signal detected. Note that the signals are reported as logarithmic values (left y-axis). Compound identity was reported when the selected ions normalized to 100% were above background signal at the peak maxima and on either side of one-half peak maxima on three consecutive scans through the chromatographic peak. In some cases, impossible ions were selected, *i.e.*, relative abundance set at 0%, which served to filter out possible matrix (background) interferant ions resulting in SIM selective detection analogous to an electron-capture detector. Fig. 2a reveals that at the temperature program employed many of the pesticides and the internal standard co-eluted. Nonetheless, SIM detection employing the MS algorithm described above provided sufficient differentiation to yield compound identity as well as semi-quantitative analyses in less than 3 min. For example, by monitoring specific ions for γ-BHC (No. 3) and [$^2H_{10}$]phenanthrene (No. 15), these two co-eluted compounds were easily differentiated. Typical signal *versus* time curves for these compounds are shown in Fig. 1b and c. Note that the four ions monitored for each compound reach the same signal height at 38 s while their relative contribution to total peak height (see Fig. 2a) are monitored separately. Retention matching, *i.e.*, $t_{R(unknown)} \leqslant t_{R(standard)} \pm 5$ s (where t_R = retention time), provides a second means for compound confirmation.

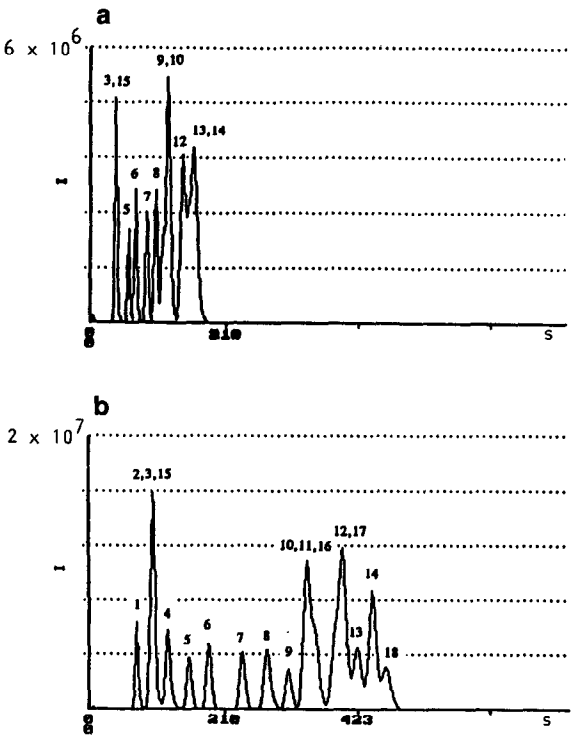

Fig. 2. Total ion current chromatograms for the same standards as shown in Fig. 1 at two different temperature programs: (a) 120 to 240°C at 18°C/min and (b) 100 to 180°C at 6°C/min. See Table II for compound identities. I = total ion current signal.

An additional advantage of SIM detection is that it provides simple visual observation of the chro-

matogram. For example, Fig. 1d shows the signal *versus* time curves for the four BHC isomers. Isomers β-BHC and γ-BHC co-elute at 38 s while α- and δ-BHC elute at 31 s and 47 s, respectively. Because the SIM reports current signal based on the peak height, visual estimation of the log response against the left y-axis can be made providing qualitative isomer concentration measurements. This approach can also be employed for the determination of the endosulfans 1 and 2. For screening level purposes, one can employ rapid GC temperature programs with SIM detection to obtain semi-quantitative or qualitative information as to pesticide presence in complex environmental samples.

For improved compound separation, a slower temperature program was employed (see Table I, program 2). Fig. 2b illustrates the separation of 17 pesticides, metabolites and internal standard. Peaks 16, 17 and 18 are endrin, endrin aldehyde and endrin ketone (endrin breakdown product), respectively. The purpose of this program was to obtain sufficient GC separation for compound identification by MS as well as to provide more quantitative analysis by TIC–SIE.

To obtain maximum TD of pesticide into the GC column and thus, optimum detection limit, a tempeature of 260°C was required. The possible breakdown of 4,4'-DDT and endrin was evaluated. Negligible breakdown was observed for DDT while endrin thermal degradation produced 30% endrin aldehyde and 64% endrin ketone. Therefore, if endrin and its metabolites are present in the sample, care must be taken when quantitative concentration assignments are made.

TABLE III

SIM AND TIC–SIE DYNAMIC RANGE AND MINIMUM DETECTABLE AMOUNT (MDA; n = 3 AT EACH CONCENTRATION)

Concentration range studied: SIM: 1000, 640, 400, 200, 10, 2, 1, 0.5, 0.2 and 0.1 ng/pesticide; TIC–SIE: 2000, 1500, 1000, 500, 50, 20 and 5 ng/pesticide except for compounds 2 and 3 which coeluted under the GC temperature program employed, 3000 to 10 ng total pesticide injected.

Compound	MDA (ng)	Slope	Intercept	r	Average signal R.S.D. (%)
SIM					
3	0.1	1918 ± 67	+20936 ± 25663	0.995	22
5	1	1377 ± 46	−27596 ± 20631	0.997	14
6	0.2	789 ± 27	+9867 ± 11018	0.995	12
7	0.5	796 ± 30	+2450 ± 12708	0.995	16
8	0.5	647 ± 14	+4883 ± 5750	0.998	12
9	2	802 ± 50	+15071 ± 23879	0.991	10
10	0.1	2904 ± 111	+22811 ± 27693	0.994	13
12	0.2	6492 ± 119	+17298 ± 48003	0.999	15
13	2	643 ± 18	+6145 ± 8590	0.998	11
14	0.5	3410 ± 129	+70677 ± 54881	0.995	14
TIC–SIE					
1	5	10529 ± 231	+272620 ± 224045	0.999	4
2 and 3	10	10052 ± 433	+730030 ± 616600	0.995	8
4	5	12384 ± 299	+367182 ± 289853	0.999	6
5	5	28059 ± 470	−1126654 ± 456386	0.999	9
6	5	17586 ± 247	+56029 ± 240179	0.999	5
7	20	8481 ± 195	+12362 ± 202103	0.999	6
8	20	8590 ± 135	+58417 ± 140079	0.999	4
9	5	11858 ± 441	−567177 ± 428517	0.996	14
10	5	66659 ± 1009	+839694 ± 980148	0.999	2
11	20	10221 ± 152	−133768 ± 157265	0.999	7
12	5	125899 ± 1527	−3364743 ± 1482553	0.9996	4
13	20	7560 ± 185	−48833 ± 192339	0.999	7
14	5	135139 ± 2810	+5557163 ± 2728885	0.999	6

TABLE IV

SIM AND TIC–SIE AVERAGE RESPONSE FACTOR (*RF*) AND THE PERCENT RELATIVE STANDARD DEVIATION

Average *RF* over the concentration range: SIM: 1000, 640, 400, 200, 100 and 10 ng/pesticide; TIC: 2000, 1500, 1000, 500, 200 and 50 ng/pesticide and for compounds β and γ-BHC, 3000, 2000, 1000, 400, 100, and 40 ng total amount injected.

Compound	SIM		TIC–SIE	
	Average RF	R.S.D. (%)	Average RF	R.S.D. (%)
α-BHC			0.070	17
β-BHC			0.076	17
γ-BHC (lindane)	0.093	18	(coetlutes with β-BHC)	
δ-BHC			0.085	18
Heptachlor	0.047	30	0.14	17
Aldrin	0.037	12	0.11	11
Heptachlor epoxide	0.031	15	0.050	13
Endosulfan 1	0.028	15	0.053	10
Dieldrin	0.038	14	0.060	9
4,4′-DDE	0.14	20	0.43	13
Endosulfan 2			0.061	8
4,4′-DDD	0.26	20	0.67	10
Endosulfan sulfate	0.028	13	0.046	13
4,4′-DDT	0.17	22	0.67	15

Differences in SIM and TIC–SIE measurement precision and detection limit were evaluated by determining their linear dynamic ranges and *RF* values. Temperature programs 1 and 2 were used for the SIM and TIC–SIE measurements, respectively. Plots of signal *versus* concentration yielded correlation coefficient, r, values closer to 1 for TIC–SIE indicating a higher degree of linearity than for SIM detection (see Table III). Moreover, the average signal R.S.D. calculated over the linear plot was typically 2–3 times lower for TIC–SIE than for SIM. Greater measurement precision was further evidenced for TIC–SIE by the lower average response factor (average *RF*) % R.S.D.s shown in Table IV.

TABLE V

COMPARISON OF INJECTED AMOUNT (10 ng/PESTICIDE) AND DETECTED PESTICIDE AMOUNT BY SIM IN THE PRESENCE OF OTHER ORGANIC COMPOUNDS (n = 3)

Compound	PCBs (10000 ng total)		A/B/N (1000 ng/compound)	
	Detected (ng)	Difference (%)	Detected (ng)	Difference (%)
3	10.0	0	8.1	−19
5	13.1	+31	18.8	+88
6	8.8	−11	10.0	0
7	8.2	−18	10.0	0
8	8.0	−20	18.5	+85
9	14.8	+48	16.9	+69
10	8.5	−15	7.9	−21
12	8.7	−13	10.0	0
13	18.5	+85	10.6	+6
14	10.7	+7	10.8	+8

Evident was the greater measurement precision obtained by TIC–SIE than from SIM. This is explained by the fact that the SIM readout is based on the logarithm of the signal measured, rounded to the nearest decimal point, as compared to TIC which provides actual current signals. For SIM, the error in the current output is highly dependent on the log value mantissa roundoff. On the other hand, the detection limit of SIM was *ca.* 30 times more sensitive.

To determine SIM selectivity, pesticide detection in the presence of significant amounts of other organic pollutants including PCBs as well as a wide variety of A/B/N organics was studied. The A/B/N standard solution contained 63 compounds comprising benzidines, phenols, PAHs, chlorinated ethers, nitrosoamines, halogenated and nitrated benzenes, phthalates and deuterated PAHs. Two experiments were conducted: standard solutions containing 10 pesticides, 10 ng/pesticide, were analyzed in the presence of (1) 10 000 ng PCBs or (2) 63 000 ng A/B/N, 1000 ng/compound. Table V illustrates the comparison of injected (thermally desorbed) *versus* detected amounts for each pesticide (n = 3 for each experiment). The percent difference for most pesticides was less than 30%. Out of the 20 measurements, 4 pesticides were over-estimated presumably due to the rise in background current as a result of matrix interference ions. Recall, that no sample cleanup was performed, that is, TDGC–SIM measurements were made in the presence of a wide range and high concentration of EPA monitored organics. It is unlikely that this level of highly contaminated sample will be present at hazardous waste or agricultural sites. Nevertheless, judicious selection of solvent-type (*i.e.*, solvent strength) should preclude many of the A/B/N organics from being extracted from soil or aqueous media. In contrast, typical EPA methods require multi-column organic fraction "cutting" for highly contaminated samples before analysis by either MS or non-descriptive, selective detectors. For example, GC–ECD analysis without pre-fractionation is unlikely to provide unabiguous pesticide identification in the presence of a wide range of chlorinated organics [12]. Therefore, the purpose of this experiment was to simulate extreme matrix interference conditions for a sample collected from a hazardous waste site.

Toward this end, a study was conducted to determine optimum solvent composition and extraction times for the puposes of providing a field-practical pesticide soil–solvent extraction. Two soil types were analyzed: soil 1 consisted of an oil stained, poorly to moderately sorted fine to medium sand and soil 2, a very poorly sorted clay to coarse sand. A variety of solvents from high to low polarity as well as some mixed solvents over a range of extraction times from 0.5 min to 20 min were studied. The bar graph shown in Fig. 3 depicts optimum pesticide recovery for the dried soils and the same soils with 10–30% moisture. For example, 4 μg/g/pesticide added to 2 g dry soil and extracted with 2 ml hexane for 2 min yielded pesticide recoveries > 90% with the exception of endosulfan sulfate whose recovery was about 65%. Decreased pesticide recovery was obtained as soil moisture content increased. Extraction with hexane–methanol (4:1, v/v) resulted in comparable recoveries as the dried soil extracted with hexane.

Five oil-stained soil 1 (2 g) samples were prepared containing 4000 to 50 ng/g/pesticide. The samples were extracted as described above and analyzed by TDGC–SIM-MS and TCGC–TIC–SIE-MS *and* GC–ECD. Several observations are apparent from Table VI. First TIC–SIE and ECD provided comparable measurement precision while SIM precision was higher but within the 40% R.S.D. obtained for

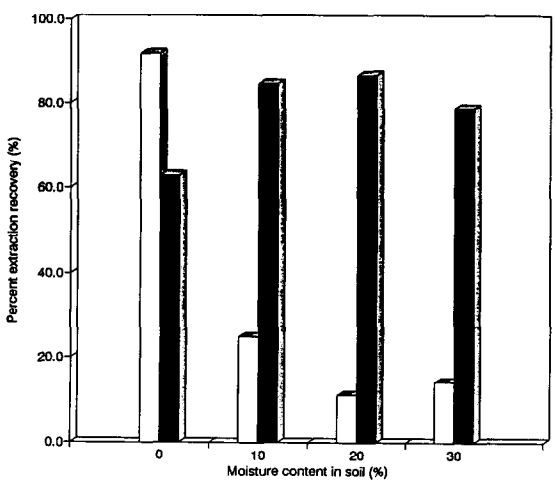

Fig. 3. Effect of soil moisture content on the average percent recovery of 10 pesticides extracted from soil 1: solvent compositions, hexane (2 ml) (open bars) and hexane–methanol (2 ml/0.5 ml) (solid bars).

TABLE VI

COMPARISON OF SIM, TIC–SIE AND GC–ECD RESULTS FOR KNOWN PESTICIDE CONCENTRATIONS IN 2 g OF SOIL 1

ND = pesticide not detected. For this experiment, no recovery data were used in the calculation of amount detected. Note that 65% extraction efficiency was found for compound 13 (endosulfan sulfate).

Compound	Detected amount, ppb (R.S.D. %[a])				
	SIM	TIC	GC–ECD	Average	R.S.D. (%)
4000 ppb/pesticide					
3	4283 (11)	4049 (3)	3739 (3)	4024	6
5	4788 (35)	4047 (7)	3715 (4)	4183	11
6	4425 (34)	4407 (5)	3617 (4)	4150	9
7	3939 (19)	4174 (4)	3735 (4)	3949	5
8	4881 (27)	4830 (4)	3808 (6)	4506	11
9	3667 (30)	4681 (5)	3583 (2)	3977	13
10	4795 (19)	4142 (6)	4042 (1)	4326	8
12	4395 (20)	4173 (6)	3803 (5)	4124	6
13	2814 (27)	2397 (7)	6475 (1)[b]	–	
14	4881 (20)	4506 (4)		–	
1000 ppb/pesticide					
3	801 (19)	941 (1)	948 (1)	897	8
5	906 (42)	904 (4)	922 (2)	911	1
6	1081 (30)	992 (4)	920 (6)	998	7
7	989 (19)	964 (3)	940 (5)	964	2
8	1098 (11)	1088 (0)	934 (7)	1040	7
9	1230 (23)	1067 (4)	987 (6)	1095	9
10	1252 (35)	998 (3)	953 (7)	1068	11
12	1194 (23)	1001 (0)	1132 (7)	1109	7
13	656 (30)	678 (3)	1606 (9)[b]	–	
14	1054 (23)	1028 (0)		–	
500 ppb/pesticide					
3	435 (20)	520 (6)	472 (16)	476	7
5	335 (10)	551 (5)	485 (14)	457	20
6	481 (0)	555 (3)	476 (11)	504	7
7	453 (10)	417 (2)	476 (13)	449	5
8	571 (10)	710 (7)	461 (12)	581	18
9	516 (0)	630 (10)	477 (13)	541	12
10	471 (0)	515 (2)	484 (13)	490	4
12	544 (11)	527 (8)	492 (14)	521	4
13	292 (0)	330 (7)	770 (25)[b]	–	
14	557 (0)	596 (5)		–	
100 ppb/pesticide					
3	92 (10)	34 (49)	98 (10)	75	39
5	98 (11)	51 (22)	100 (12)	83	27
6	89 (10)	ND	93 (13)	–	
7	99 (19)	ND	99 (15)	–	
8	96 (11)[c]	ND	87 (17)	–	
9	100 (23)[c]	ND	100 (23)	–	
10	96 (19)	96 (16)	102 (21)	98	3
12	109 (11)	121 (18)	97 (27)	109	9
13	70 (23)	ND	152 (29)[b]	–	
14	168 (23)[c]	111 (6)		–	

(Continued on p. 286)

TABLE VI *(continued)*

Compound	Detected amount, ppb (R.S.D. %[a])				
	SIM	TIC	GC–ECD	Average	R.S.D. (%)
50 ppb/pesticide					
3	47 (23)	10 (62)	49 (3)	35	51
5	45 (0)	ND	58 (3)	–	
6	46 (23)	ND	50 (1)	–	
7	39 (19)	ND	52 (1)	–	
8	49 (20)[c]	ND	48 (3)	–	
9	42 (0)[c]	ND	54 (1)	–	
10	41 (11)	37 (31)	54 (4)	44	16
12	48 (23)	45 (40)	50 (9)	48	4
13	32 (11)	ND	89 (8)[b]	–	
14	72 (19)[c]	50 (20)		–	

[a] n = 3 for SIM, TIC, GC–ECD.
[b] Pesticides 13 and 14 co-eluted by GC–ECD, therefore, the average and R.S.D. were not calculated.
[c] Detected amount calculated using one-point RF calibration

the standard solution linear dynamic range of *RF* studies. In general, TIC–SIE produced better run-to-run measurement precision, *ca.* 5% R.S.D., than

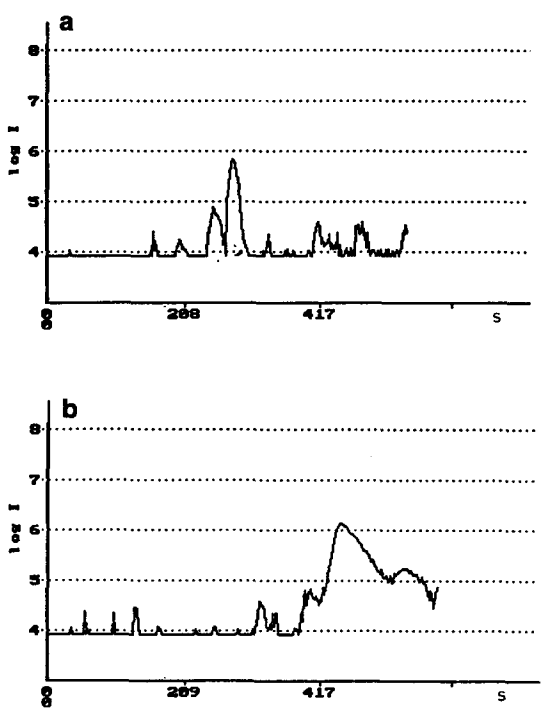

Fig. 4. Total ion current chromatograms of hexane—C_{18} extracted pond (a) and sea (b) waters. Temperature program: 100 to 180°C at 6°C/min. I = total ion current.

did SIM, *ca.* 20% R.S.D. Second, as anticipated SIM provided increased sensntivity over TIC–SIE. However, compounds 8, 9 and 14 were over-estimated at the lower pesticide concentrations using the linear dynamic range *RF* value. These concentrations are near the SIM detection limit. Over-estimation occurs presumably due to log current roundoff as a function of decreased analyte signal-to-noise ratio and the *RF* falling outside the linear dynamic range at these concentrations. For a more quantitative SIM measurement, a "one-point" *RF* calibration can be made. For example, by calculating the *RF* value of endosulfan 1 at an injection amount of 2.5 ng, the SIM measurement for the 100 ppb and 50 ppb samples yielded 96 ± 11 ppb and 49 ± 10 ppb, respectively. Third, the average pesticide concentration R.S.D. calculated from the SIM, TIC–SIE and ECD detected amounts were well-within the acceptable range for intermethod comparisons [14,15].

SPE using a C_{18} bonded phase silica cartridge was employed as a field-practical means for extracting pesticides from aqueous samples. To test the method, known amounts of pesticide were added to 500 ml deionized water and passed through the cartridge at a rate of 90–130 ml/min. The pesticides were eluted off the cartridge with hexane and collected in the first 1 ml. The extraction procedure was repeated three times and each extract analyzed three times. Table VII lists the SPE recoveries for

TABLE VII

PESTICIDE PERCENT RECOVERY (%) OF DEIONIZED WATER–C_{18} SOLID-PHASE EXTRACTION WITH SIM DETECTION

For each concentration 3 extractions were prepared and each extract analyzed 3 times; ND = not detected.

Compound	Pesticide concentration (ng/l)						
	40[a]	100[a]	2000	6000	10000	20000	Average (R.S.D., %)
3	81 ± 5	95 ± 6	68 ± 19	55 ± 9	55 ± 9	54 ± 5	68 (23)
5	69 ± 8	86 ± 18	69 ± 9	79 ± 18	71 ± 1	83 ± 12	76 (9)
6	67 ± 17	89 ± 14	85 ± 13	72 ± 12	67 ± 5	73 ± 6	76 (11)
7	61 ± 24	77 ± 17	92 ± 14	91 ± 18	82 ± 19	100 ± 13	84 (15)
8	ND	93 ± 15	93 ± 5	96 ± 12	85 ± 16	96 ± 14	93 (5)
9	ND	94 ± 16	98 ± 25	96 ± 8	95 ± 4	115 ± 13	100 (9)
10	93 ± 25	77 ± 6	84 ± 13	91 ± 3	65 ± 8	62 ± 7	79 (15)
12	106 ± 17	86 ± 6	96 ± 16	92 ± 12	71 ± 5	87 ± 7	90 (12)
13	ND	77 ± 11	75 ± 9	81 ± 8	70 ± 5	97 ± 9	80 (13)
14	126 ± 18	108 ± 25	78 ± 10	70 ± 7	73 ± 13	67 ± 9	87 (25)

[a] Calculated using one-point *RF* calibration.

the pesticides between the concentration range of 20 000 ng/l and 100 ng/l for each pesticide. At each concentration, the SIM measurement precision was $< 25\%$ ($n = 9$) and the average recovery R.S.D. over the concentration range was $< 30\%$ ($n = 54$). The average recovery R.S.Ds over the concentration range studied suggest that the pesticide recoveries were linear. This was evident by the plots of the average SIM signal *versus* concentration which yielded $r > 0.996$.

Pond and sea water samples were collected, filtered and analyzed as field blanks. Shown in Fig. 4 are the TIC chromatograms for both the pond and sea waters: apparent are the presence of organics eluting during the retention times of interest. Pesticides were added to the water at 2000 ng/l per compound (500 ml). The pesticide average recovery value shown in Table VII was used in the calculation. Table VIII illustrates the SIM detected amount and percent differences after SPE. The percent differ-

TABLE VIII

COMPARISON OF FORTIFIED AND SIM DETECTED AMOUNTS OF PESTICIDES FROM POND AND SEA WATER SAMPLES: FORTIFIED CONCENTRATION 2000 ng/l PER PESTICIDE

The water samples were extracted 3 times and each extract analyzed 3 times.

Compound	Pond water		Sea water	
	Detected (ng/l)	Difference (%)	Detected (ng/l)	Difference (%)
3	2324 ± 147	+16	2412 ± 470	+21
5	2053 ± 237	+3	1806 ± 184	−10
6	2000 ± 369	0	2369 ± 211	+18
7	2428 ± 309	+21	2310 ± 357	+16
8	2946 ± 258	+47	2129 ± 237	+6
9	2160 ± 220	+8	2240 ± 220	+12
10	2278 ± 127	+14	1924 ± 51	−4
12	2311 ± 89	+16	2200 ± 289	+10
13	2150 ± 350	+8	1900 ± 400	−5
14	1701 ± 0	−15	1701 ± 245	−15

ence was within 30% for all of the pesticides except endosulfan 1 in pond water. Experiments at the 40 ng/l per pesticide levels indicated that all of the pesticides were detected with the same method precision as above with the exception of dieldrin, endosulfan 1, and endosulfan sulfate whose concentrations were at the SIM detection limit.

The results of a 6-commercial laboratory GC–MS detection study of chlorinated pesticides were reported [7]. Uniform calibration solutions and EPA standardized analytical procedures were followed. Five soil sediment samples were prepared to contain known concentrations of pesticides with the exception of 1 sample. Two different sample cleanup procedures for solids were employed resulting in duplicates of 4 different extracts, *viz.*, mechanical shaking and/or ultrasonication followed by Florisil and/or gel permeation chromatography fractionation. The solid samples, fortified to contain 0.2–20 ppm/pesticide (in 10 to 50 g), had mean R.S.Ds typically between 10 and 70% with several > 100%. These findings were consistent with the reported results for multilaboratory studies of PCB and PAH soil sediment samples [7,14–17]. Although this paper does not provide data with respect to interlaboratory comparisons, the SIM, TIC–SIE and ECD produced average concentration measurement precision well-within the multilaboratory R.S.Ds reported above and over a much wider pesticide/soil concentration range. In addition to the solids results described above, the authors conducted a multilaboratory GC–MS comparison study for the detection of pesticides fortified, 3–30 μg/l, in water. Water samples were prepared for analysis by performing several liquid–liquid extraction steps. The 6-commercial laboratory measured mean concentration R.S.D.s for 2 different water samples were found to be between 30 and 60%. Although the results reported in Table VII in this paper are not based on multiple laboratory or method comparisons, the SIM average measured concentration R.S.D.s over the concentration range studied were well under the 6-laboratory R.S.D. range and suggests that multimethod precision should be no worse than the soil results shown in Table VI.

Semi-quantitative TDGC–SIM-MS as well as more quantitative TIC–SIE measurements have been developed for field detection of organochlorine pesticides in soil and water. In general, SIM produced < 40% measurement precision with analysis times of less than 3 min/sample while TIC–SIE produces data comparable to standardized EPA methods (*i.e.*, < 30% R.S.D.). Although SIM measurement precision was somewhat less than TIC–SIE, measurement accuracies were comparable. The ability to obtain rapid, on-site chemical data should support activities in hazardous waste site assessment *and* routine regulatory programs in environmental and agricultural monitoring.

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