Static Headspace and Gas Chromatographic Analysis of Fumigant Residues in Soil and Water

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Soil fumigants are characterized by high vapor pressures and low boiling points, which determine that the commonly used solvent extraction-based methods are not suitable for sample preparation. The paper reports static headspace gas chromatography (GC) methods for the analysis of the fumigants 1,3-dichloropropene (1,3-D) and methyl isothiocyanate (MITC) in soil and water. Method optimization was achieved by modifying the sample matrix with concentrated salt solution and adjusting sample equilibration temperature and time on the headspace autosampler. The headspace GC methods showed ~1 order of magnitude greater GC response than a cold solvent extraction method under the same GC conditions and also gave cleaner chromatograms and more stable baselines. When applied to soil samples taken from a fumigated field, the headspacee GC method showed reproducibility similar to that of a solvent extraction method but had an improved detectability for deep-layer samples that contained low levels of 1,3-D.

Keywords: *Headspace analysis; static headspace analysis; fumigants; 1,3-dichloropropene; methyl isothiocyanate*

INTRODUCTION

In recent years, soil fumigants have attracted broad attention because of their detrimental health and environmental effects. The use of many fumigants, including 1,2-dibromo-3-chloropropane (DBCP), ethylene dibromide (EDB), and methyl bromide, has been or will soon be discontinued in various regions (Noling and Becker, 1994; UNEP, 1995). The few remaining fumigants, primarily 1,3-dichloropropene (1,3-D) and methyl isothiocyanate (MITC), are similar to the banned chemicals in that they also move rapidly in the soil (Leistra, 1970; McKenry and Thomason, 1974; Schneider et al., 1995) and are suspected carcinogens (Baker et al., 1996). More extensive monitoring of these fumigants in the environment requires the use of speedy and sensitive analytical methods.

Both 1,3-D and MITC have very low boiling points (104−114 °C for 1,3-D isomers and 119 °C for MITC) and high vapor pressures (4.5−5.7 kPa for 1,3-D isomers and 2.8 kPa for MITC at 20 °C). Because of their high volatility, the commonly used solvent extraction-based sample preparation methods, such as Soxhlet extraction, cold solvent extraction (e.g., shaking), and solid-phase extraction, are not suitable for recovering their residues from soil or water. First, low and inconsistent recoveries may result from volatilization losses of the analyte during sample preparation. Second, as the solvent extract cannot be concentrated using vacuum evaporation or solid-phase extraction, the sensitivity of analysis will be low. Third, the extract cannot be cleaned up to minimize interference, as cleanup procedures such as solid-phase adsorption and solvent−solvent partitioning may result in further volatilization losses. One method that can potentially eliminate these drawbacks is headspace gas chromatographic (GC) analysis.

In automated static headspace GC analysis (HS-GC), a sample is thermally equilibrated in a closed headspace vial, and an aliquot of the headspace is introduced into the GC column. Static headspace methods have found frequent applications in flavor analysis in food industries (Girard and Nakai, 1991), detection of alcohol in blood (Seto, 1994), monitoring of volatiles in air (Canela and Muehleisen, 1988), and analysis of solvent residues in pharmaceuticals (Russo, 1994; George and Wright, 1997) and volatile contaminants in water or waste effluents (Gryder-Boutet and Kennish, 1988). It has also been applied to the analysis of fumigants in food (Norman, 1991) or adsorbed on activated carbon samplers (Woodrow et al., 1988; Gan et al., 1994, 1995). In contrast to dynamic headspace analysis (i.e., purge and trap), static HS-GC analysis is more rapid and, when optimized, may provide sensitivity comparable to that of the former (Wylie, 1988; Voice and Kolb, 1993). The use of static HS-GC methods for analyzing volatile compounds in soil is relatively rare (Voice and Kolb, 1993; Kolb, 1996). Applications of static HS-GC methods for the analysis of volatile pesticide residues in soil or water have not been reported.

In this paper, we report optimized static HS-GC methods for analyzing residues of fumigant 1,3-D and MITC in soil and water samples. Method optimization was achieved by maximizing sensitivity through modifying the matrix and selecting optimum sample equilibration conditions on a headspace autosampler. The optimized static HS-GC method was applied to the analysis of 1,3-D residues in soil samples taken from a fumigated field.

MATERIALS AND METHODS

Fumigant Standards and Soil. Analytical standards of 1,3-D and MITC were purchased from Chem Service Co. (West

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Chester, PA) and had purity of >99%. The 1,3-D standard was a mixture of the *Z* (48%) and *E* (50%) isomers. An Arlington sandy loam (mixed, hyperthermic Typic Torripsamments) from a field at the Agricultural Experiment Station, University of California, Riverside, was used in the optimization of static HS-GC methods. The same field was later fumigated with 1,3-D by chisel injection. The soil had a 0.92% organic matter content (OM) and pH of 7.2. The soil was air-dried and then passed through a 2-mm sieve before use.

Matrix Modification. The first step in method optimization was the modification of the sample matrix to increase partitioning into the headspace so that the sensitivity of analysis was maximized. This was achieved through addition of a concentrated salt solution to a soil sample or addition of salt to a water sample in the headspace vial. The type and concentration of salt, as well as the volume of salt solution, were selected through stepwise optimization.

Soil. Eleven grams of Arlington soil (adjusted to 10% moisture content) was weighed into 20-mL headspace vials (Supelco Co., Bellefonte, PA), and 50 μg of 1,3-D and 50 μg of MITC in 5 μL of acetone were added using a gastight syringe. The spiked soil vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa (Supelco) and chilled at −15 °C for at least 1 h. The sample vials were then decapped, and 5.0 mL of deionized water or solution containing 20% (w/v) NaCl, Na_2CO_3, $NaNO_3$, or $(NH_4)_2SO_4$ was added, followed by immediate recapping. Six replicates for each solution type were analyzed on a Tekmar 7000 automated headspace sampler (Tekmar Co., Cincinnati, OH) in tandem with an HP 5890 GC (Fresno, CA). The headspace conditions were as follows: 1.0-mL sample loop; 90 °C sample equilibration temperature; 15-min sample equilibration time; 0.5-min mixing time (at power 10); 110-kPa vial pressurization pressure; and 0.5-min injection time. After the sample was introduced into the GC column, the column flow was split into two flows before entering the detectors by using a Y-shaped quartz connector. One flow was introduced into an electron capture detector (ECD) for the detection of 1,3-D isomers and the other into a nitrogen and phosphorus detector (NPD) for the detection of MITC. The GC conditions were as follows: RTX-624 capillary column (30 m × 0.25 mm × 1.4 μm, Restek Co., Bellefonte, PA); 240 °C inlet temperature; 300 °C detector temperature for both detectors; 80 °C isothermal oven temperature; and 1.1 mL/min column flow rate. The salt that produced the greatest GC responses in area was selected as the best salt type for modifying the matrix.

Using the selected salt, the optimum concentration and volume of the salt solution were determined. To select the optimum salt concentration, the concentration was varied from 0 to near saturation (30% w/v) while the volume of solution was maintained at 5.0 mL. To determine the optimum volume, the volume of solution was varied from 2 to 11 mL while the concentration was maintained at the optimum value. Six replicates were included for each concentration or volume, and the same HS-GC conditions as described above were used. The optimum value was defined as the condition that resulted in the greatest and/or the most reproducible GC responses.

Water. Optimization strategies similar to that for soil samples were used to determine the optimum matrix conditions for water. Water samples were obtained by shaking 400 g of Arlington soil in 2000 mL of deionized water and collecting the supernatant after centrifugation. To optimize the type and concentration of matrix-modifying salt, 10.0 mL of water in headspace vials was spiked with 1.0 μg of 1,3-D and 1.0 μg of MITC in 5 μL of water to arrive at an initial concentration of 0.1 μg/mL. After the capped samples were chilled, different salts were added to arrive at a salt concentration of 20% (w/v). Six replicated samples were analyzed on the headspace-GC system using the same conditions as given for soil samples. The best salt type was selected as the one that gave the greatest GC response. The optimum concentration of salt was subsequently determined by modifying the spikes with different concentrations of the selected salt and evaluating GC responses.

Headspace Conditions. Among the conditions that may affect the sensitivity of static HS-GC analysis using an automated headspace sampler, sample equilibration temperature and time are the most important (Friant and Suffet, 1979; Penton, 1992; Gan et al., 1994, 1995). To determine the optimum equilibration temperature for soil and water samples, six replicated samples were equilibrated on the headspace autosampler for the same time period (15 min) but at different temperatures. The temperature was incrementally (by 5 °C) varied from 70 to 95 °C for the soil samples and from 60 to 95 °C for the water samples. The temperature that gave the greatest GC response was selected as the optimum sample equilibration temperature. The optimum equilibration time was similarly determined by varying the sample heating cycle for intervals of 5, 10, 15, 20, 30, and 45 min.

Method Evaluation. Method evaluation was made by comparing the sensitivity of static HS-GC methods with that of a solvent extraction method and by applying both methods to the analysis of soils sampled from a 1,3-D-treated field. To compare the sensitivities, standard curves were generated using different methods under the same GC conditions, and the slope of the linearized curves was subjected to a paired *t* test. The solvent extraction method was modified from procedures previously used for the analysis of 1,3-D and MITC in laboratory and field soil samples (van der Pas and Leistra, 1978; Boeston et al., 1991; Ou et al., 1995; Schneider et al., 1995). For soil samples, soil (10 g dry weight, with 10% moisture) was spiked with various amounts of 1,3-D and MITC and extracted with 10 mL of ethyl acetate in closed vials by shaking at high speed for 2 h. An aliquot (2 μL) of the extract was injected into the GC after the residual water in the solvent phase was removed by anhydrous sodium sulfate. For water samples, 10 mL of water spiked with different amounts of 1,3-D and MITC was extracted with 10 mL of ethyl acetate in a closed vial. Samples were shaken for 2 h at high speed, and 2 μL of the solvent phase was injected into the GC after the residual water was removed.

Soil samples were obtained from a field 24 h after a commercial formulation of 1,3-D, Telone II (DowElanco, Indianapolis, IN), was injected at a depth of 30 cm into the center of 100-cm-wide beds. Samples were collected from the center of a treated bed using a hand auger, and samples from different depths were collected. To minimize volatilization loss during sampling, soil samples were directly transferred from the auger into chilled Mason jars, and the jars were immediately closed with metal lids, followed by additional sealing around the lid with adhesive aluminum tape. The soil samples were then stored at −15 °C until analysis. To analyze 1,3-D concentrations in the soil, soil samples were thawed and thoroughly mixed in the closed jars. After the soil moisture content was determined, subsamples from the same jar were removed and analyzed by using the static HS-GC method and the solvent extraction method. In headspace analysis, the calibration table was made by spiking untreated soil (adjusted to the same moisture content as in field samples) with known amounts of 1,3-D standard and analyzing under the same conditions.

RESULTS AND DISCUSSION

Optimized Headspace GC Methods for Soil. The GC output showed a close dependence on the type, concentration, and volume of the matrix-modifying salt solution when soil spikes were analyzed according to the static HS-GC method. Substituting deionized water with 20% NaCl or $NaNO_3$ solution significantly increased the GC response, and the enhancement was greater for MITC than for 1,3-D isomers (Figure 1). Addition of Na_2CO_3 reduced the response for MITC, and addition of $(NH_4)_2SO_4$ greatly reduced the response for both MITC and 1,3-D. On the basis of the relative response, NaCl was selected as the best salt type for modifying soil samples for both MITC and 1,3-D iso-

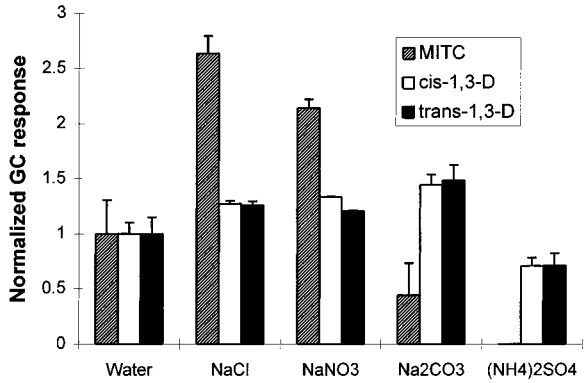

Figure 1. Effect of salt type on GC response for 10-g soil samples spiked with 1,3-D and MITC. The concentration of each salt solution was 20% (w/v), and the error bar was calculated from six replicates.

mers. The GC response increased as the concentration of NaCl was increased from 0 to 30% (w/v), and the relative increase was greater for MITC than for 1,3-D isomers. For instance, with the addition of 30% NaCl solution, the GC response for MITC increased by 4.8 times, while that for 1,3-D isomers increased by 1.5 times, over that for water. Concentrations >30% were not tested, as NaCl solution approached saturation with further concentration increases. The optimum NaCl concentration was thus determined as 30%. The GC response decreased as the amount of 30% NaCl solution was increased from 2 to 11 mL. However, more variations were observed when only 2 or 3 mL of NaCl solution was used, and 5 mL was thus selected as the optimum solution volume.

Using 5 mL of 30% NaCl as the matrix-modifying solution, the static HS-GC method was further optimized by adjusting the equilibration temperature and time on the headspace autosampler (Figure 2). As the temperature was increased, the GC response for both MITC and 1,3-D first increased and then decreased (Figure 2a). The GC responses for both MITC and 1,3-D isomers were greatest at 85 °C. As the equilibration time was increased while the temperature was held constant at 85 °C, the GC response for both MITC and 1,3-D isomers first increased and then decreased (Figure 2b). The greatest response was observed with 30 min of equilibration. The optimum conditions for headspace GC analysis of MITC and 1,3-D isomers in soil are summarized in Table 1.

The effect of adding salt to the sample matrix on GC response was attributed to a "salting out" effect (Penton, 1992; Seto, 1994). Some salts, such as Na_2CO_3 and $(NH_4)_2SO_4$, however, showed a negative effect on the signal output of MITC or 1,3-D compared to water, and the extent of signal reduction indicates that fumigant degradation by these salts may have occurred at the elevated temperature. Our study also showed that salt addition had different effects for different compounds, but the physical or chemical properties that contributed to this difference were not identified.

The dependence of sensitivity on sample equilibration temperature and time may be explained by the interactions of these variables with the equilibrium of the analyte among the three phases. Higher temperature and longer time facilitate the partitioning of an analyte from the solid phase into the aqueous phase and from the aqueous phase into the headspace, thus enhancing the sensitivity of analysis. On the other hand, however,

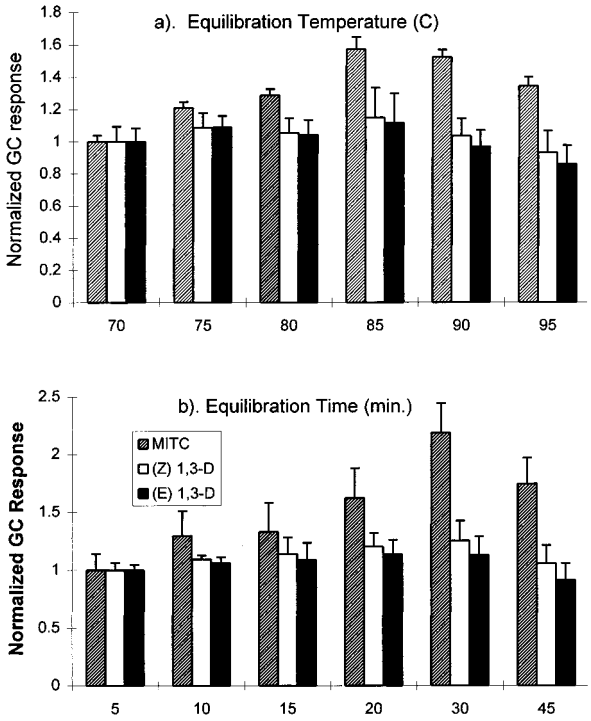

Figure 2. Effect of headspace sampler conditions on GC response for 10-g soil samples spiked with 1,3-D and MITC: (a) sample equilibration temperature (°C); (b) sample equilibration time (min). Error bars are calculated from six replicates.

Table 1. Optimized Conditions of Headspace GC Methods for Analysis of 1,3-D and MITC in Soil and Water Samples[a]

	soil (10 g)		water (10 mL)	
parameter	MITC	1,3-D	MITC	1,3-D
salt type	NaCl	NaCl	NaCl	NaCl
concentration (%, w/v)	30	30	25	25
volume (mL)	5	5		
equilibrn temperature (°C)	85	85	80	80
equilibrn time (min)	30	30	20	25

[a] Analysis was performed on a Tekmar 7000 automated headspace autosampler using a 1.0-mL sample loop and 20-mL headspace vials.

Table 2. Ratios of GC Response from the Headspace GC Method and GC Response from the Solvent Extraction Method (n = 10)

sample type	MITC	*Z*-1,3-D	*E*-1,3-D
water	8.1 ± 1.0	15.5 ± 1.2	12.9 ± 1.6
soil	8.5 ± 2.0	10.9 ± 1.6	9.5 ± 1.4

high temperature and prolonged equilibration may cause the decomposition of the analyte. Similar dependence of signal output on headspace variables were also observed in other studies, including 1,3-D and MITC on activated carbon (Gan et al., 1994).

Optimized Headspace GC Methods for Water. The effects of matrix conditions and headspace parameters on the GC response of water samples were generally similar to those found with soil samples, except that the optimum points were reached at a lower salt concentration (25%), a lower equilibration temperature (80 °C), and a shorter equilibration time (20 min). The slight differences may be due to the fact that in a headspace vial containing water, only two phases are involved. Also, the rate or mechanism of degradation of the analyte may be different from that of a headspace

Table 3. Soil Concentrations (Micrograms per Gram) of 1,3-D Determined by Using a Cold Solvent Extraction Method and a Headspace GC Method ($n = 4$) for Soil Samples Collected from a Field Fumigated with 1,3-D

	Z-1,3-D		*E*-1,3-D	
depth (cm)	solvent extraction	HS-GC	solvent extraction	HS-GC
0−25	0.753 ± 0.147	0.625 ± 0.108	2.600 ± 0.547	2.064 ± 0.387
26−30	0.369 ± 0.058	0.576 ± 0.029[a]	1.310 ± 0.162	1.549 ± 0.069[a]
31−40	0.576 ± 0.033	0.661 ± 0.040[a]	1.024 ± 0.058	0.941 ± 1.024
41−50	0.166 ± 0.011	0.203 ± 0.054	0.183 ± 0.010	0.173 ± 0.047
51−60	0.024 ± 0.001	0.042 ± 0.004[a]	0.044 ± 0.003	0.057 ± 0.007[a]
61−70	ND	0.011 ± 0.003[a]	ND	0.015 ± 0.006[a]

[a] The concentration determined by the HS-GC method was significantly greater ($\alpha = 0.05$) than that determined by the solvent extraction method.

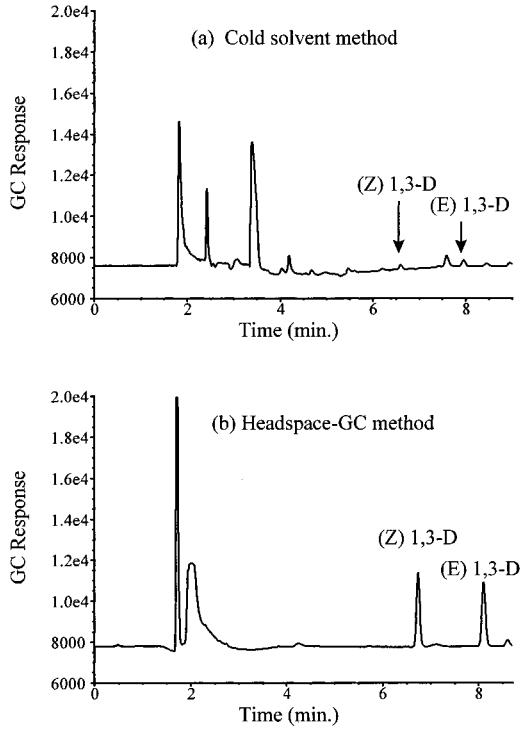

Figure 3. Gas chromatograms of soil samples taken from 51−60 cm in a 1,3-D-treated field: (a) analysis following ethyl acetate extraction; (b) headspace GC analysis.

vial containing soil. The optimum conditions for headspace analysis of MITC and 1,3-D in water samples are summarized in Table 1.

Method Evaluation. Under identical GC conditions, headspace analysis was consistently ~1 order of magnitude more sensitive than the analysis following solvent extraction using ethyl acetate, and the difference was significant ($\alpha = 0.01$) for all of the comparisons (Table 2). The improved sensitivity of static HS-GC analysis was a result of lesser dilution of the analyte, as the conditions established in a headspace vial favored the enrichment of the analyte in the headspace, of which a fraction was analyzed. In the solvent extraction-based analysis, as only 2 μL of the 10 mL of ethyl acetate extract was injected into the GC, the dilution factor was 5000 times. Although no effort was made to optimize the conditions for the solvent extraction method, the conditions were similar to those used in previous studies (Boesten et al., 1991; Schneider et al., 1995), and the injected volume (2 μL) and amount of extracting solvent (10 mL) were considered appropriate for the GC and sample conditions used in this study.

Soil samples taken from 0 to 70 cm in a 1,3-D-treated field were simultaneously analyzed by the static HS-GC method and the solvent extraction method, and the results are shown in Table 3. The concentrations from the static HS-GC analysis were similar to those obtained by using the solvent extraction method for the samples from 0−25-, 31−40-, and 41−50-cm layers but were significantly higher ($\alpha = 0.05$) for the 26−30-, 51−60-, and 61−70-cm layers (Table 3). For the samples from the deepest layer (61−70 cm), the solvent extraction method failed to detect the presence of 1,3-D, while the HS-GC method was able to give positive detections (Table 3). It was also observed that the HS-GC analysis consistently generated chromatograms with fewer unidentified peaks and a more stable baseline. Chromatograms for the 51−60-cm samples are shown in Figure 3, where the *y*-axis (GC response) was adjusted to the same range to facilitate comparison between the two methods. Under the same GC conditions, the static HS-GC chromatogram shows much stronger 1,3-D peak signals, fewer unidentified background peaks, and a more stable baseline. The cleaner chromatogram and more stable baseline in HS-GC analysis can be attributed to the fact that only readily volatile compositions from the sample matrix can enter the GC column. In addition, the static HS-GC analysis required much less time and fewer steps compared to the solvent extraction method, and no organic solvent was used. The only steps used in the headspace HS-GC analysis were transferring soil sample into the headspace vial and adding matrix-modifying solution. The improved sensitivity and sample throughput, and the elimination of solvent use, together suggest that when the number of samples is large or the concentrations of fumigants are low, the static HS-GC method will be a better method.

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