Automated headspace analysis of fumigants 1,3-dichloropropene and methyl isothiocyanate on charcoal sampling tubes

Jianying Gan* Scott R. Yates, William F. Spencer, Marylynn V. Yates

US Department of Agriculture–Agricultural Research Service Pesticide and Water Quality Research Unit, Department of Soil and Environmental Sciences, University of California, Riverside, CA 92521, USA

Abstract

Charcoal tubes are widely used for collecting organic vapor in the atmosphere, and the measurement is usually completed by analyzing an aliquot of the solvent phase following solvent extraction, typically with carbon disulfide. However, the sensitivity of this method is limited and sometimes too low for monitoring contaminants at trace levels in the environmental atmosphere. In this study, the potential of static headspace analysis techniques was explored on two common fumigants, 1,3-dichloropropene (1,3-DCP) and methyl isothiocyanate (MITC), on both coconut- and petroleum-based charcoal sampling tubes, using an automated and programmable headspace sampler. Three important parameters in the headspace analysis, equilibrating temperature and time, and amount of extracting solvent, were optimized individually for each compound–charcoal tube combination to achieve maximum sensitivity of GC analysis. Higher stability was observed for both isomers of 1,3-DCP and MITC on petroleum-based charcoal, and 180 and 190°C, and 5 min were selected as the equilibrating temperatures and time, respectively. On coconut-based charcoal tubes, however, all the compounds were more sensitive to the temperature, and 160 and 140°C, and 5.0 and 3.0 min were therefore determined as the equilibrating temperatures and times for the 1,3-DCP isomers and MITC, respectively. Reducing solvent volume from 3 to 1 ml in 9-ml headspace vials improved the sensitivity and 1.0 ml benzyl alcohol was therefore selected for all the compound–charcoal tube combinations. Compared to the conventional extraction method with CS_2, the optimized headspace methods were 10–35 times more sensitive, and equivalently reproducible except for MITC on coconut-based ORBO-32 tubes. Better sensitivity and precision of measurements were consistently obtained on petroleum-based charcoal tubes, and the minimum detection limits were estimated as 0.2 and 0.5 ng per tube for the (Z)- and (E)-isomers of 1,3-DCP, respectively, and 2.0 ng per tube for MITC. With the automated headspace method, sample preparation was simplified and sample throughput was greatly enhanced, and up to 200 samples could be analyzed on a 24-h basis under the optimum conditions.

1. Introduction

The (Z)- and (E)-isomers of 1,3-dichloro-

---

* Corresponding author.

propene (1,3-DCP) and metham-sodium (sodium N-methyldithiocarbamate) are widely used as soil fumigants for parasitic plant nematodes [1,2].

In soil, metham-sodium decomposes quickly to produce methyl isothiocyanate (MITC) [3]. A

significant fraction of the applied fumigants may diffuse up to the soil surface and escape into the atmosphere as organic vapor due to their extremely high vapor pressures [4]. As found with chlorofluorocarbons, methyl chloroform, halons and methyl bromide, many chlorine and bromine-containing compounds may possess the power of ozone destruction. The continuation of the soil-disinfection practice using these fumigants may largely rely on the extent of their emission into the atmosphere and the possible adverse impact on the environment. To monitor the behavior of 1,3-DCP and MITC after application, methods of sampling and analysis with high sensitivity and sample throughput need to be developed.

Though many sampling methods such as solvent scrubbing and cryogenic concentration exist, solid adsorption is the most effective and widely used method for collecting organic contaminants in the atmosphere [5]. Two basic types of solid adsorbent are commonly used. The more traditional method, used in many procedures recommended by the National Institute for Occupational Safety and Health (NIOSH), utilizes charcoal as the adsorbent, followed by solvent desorption and GC analysis of an aliquot of the solvent extract [5,6]. The other method uses porous polymer adsorbents, such as Tenax and polyurethane foams. Direct thermal desorption into the GC system is commonly used for Tenax, while exhaustive solvent extraction, usually Soxhlet extraction, is used for polyurethane foams [5,7,8]. Both methods have advantages and disadvantages. Collection using charcoal tubes usually allows high flow-rates and large sampling volumes, and charcoal sampling tubes are inexpensive and easy to handle both in the field and in the laboratory [9]. However, since only a few μl of the entire solvent extract (a few ml) are injected into the GC system, two to three orders of magnitude dilution is often involved, which results in relatively low sensitivity of detection for this method. Besides, the interferences from solvent and the dissolved impurities are sometimes also disadvantages. With Tenax and thermal desorption, since the entire or main portion of the sample is introduced into

the GC system, the sensitivity of analysis is usually high. However, sampling tubes packed with Tenax-GC (or other types of Tenax) only allows small safe sampling volumes and low flow-rates, especially for compounds with low boiling points, for which the sampling volumes are often limited to < 1 l and flow-rates to < 50 ml min^{-1} [7]. Tenax is expensive and conditioning prior to installation is usually required. Sample stability on Tenax is sometimes also poor, and each analysis is destructive and usually takes long time which results in low sample throughput [10]. Soxhlet extraction of samples on polyurethane foams is time and solvent consuming, and the impurities are extracted together with the interested compounds. Therefore, improvements leading to better analytical sensitivity for air samples on charcoal tubes are highly desirable and of great practical importance.

Measurement of interested analytes from the vapor phase in the headspace in a closed system instead of directly from the sample matrix, i.e., headspace analysis, has been extensively used in the qualitative and quantitative determination of chemical residues and flavors in food products [11,12], and pollutants in water and other aqueous solutions [13,14] and soil and other solids [15,16]. Headspace analysis eliminates the entry of sample solution or solvent and the interfering non- or semi-volatile impurities into the GC column, simplifies the sample preparation process, and often offers better sensitivity for the analysis of volatile compounds. Jentzsch et al. [17] and Kolb [18] first reported the use of an electropneumatic dosing device in the place of a manual gas-tight syringe to automate some of the steps in their headspace-GC applications. Automated dynamic headspace samplers, or purge-and-trap systems, and static headspace samplers, have become commercially available, which provide enhanced precision and sample throughput through the automation. However, so far very little effort has been made to investigate the applicability of headspace analysis techniques in analyzing air samples on charcoal adsorbents [19,20].

Charcoals of two different origins, coconut-based and petroleum-based, are currently used

in packing charcoal sampling tubes. Charcoal in a glass tubing is divided into a larger front adsorption bed (A) and a smaller backup adsorption bed (B) with glass wool plugs and glass wool or polyurethane spacers. Charcoal tubes with this type of configuration are generally classified as ORBO tubes [5]. Different types of ORBO tubes are recommended for different compounds by NIOSH [5]. Use of charcoal tubes for the sampling of fumigants in air has been reported for 1,3-DCP and MITC, and the safe flow-rates and sampling volumes which did not cause any significant breakthrough have been well defined [21,22]. However, in those studies, solvent desorption with CS_2 or other solvents (such as acetone and benzene) was used, and the sensitivity of analysis and sample throughput were relatively low. The reported best minimum detection limits (MDLs) were 0.2 μg m^{-3} for 1,3-DCP and 1.0 μg m^{-3} for MITC when 40 l of air were sampled [21]. These limits may be sufficient for monitoring the atmosphere at workplaces, but not high enough for environmental monitoring in the field.

In this paper, headspace analysis methods for the (Z)- and (E)-isomers of 1,3-DCP and MITC using a static headspace autosampler are reported. Conditions including the equilibrating temperature and time, and solvent volume, were optimized to generate maximum sensitivity and precision of measurement. The sensitivity and precision of measurements using the optimized headspace methods were compared to the conventional solvent extraction method using CS_2 as the solvent.

2. Experimental[1]

2.1. Chemicals and ORBO tubes

Standard of 1,3-DCP in a mixture of the (Z)- (71%) and (E)- (27%) isomers was purchased

---

from Chem Service (West Chester, PA, USA). MITC standard was purchased from Sigma (St. Louis, MO, USA) with a purity of >99.0%. Benzyl alcohol and carbon disulfide were all from Fisher Scientific (Fair Lawn, NJ, USA) and used without further purification.

Two types of charcoal sampling tubes, coconut-based ORBO-32 and petroleum-based ORBO-306, were purchased from Supelco (Bellefonte, PA, USA). Both tubes had the same configuration, and 600 mg charcoal (20–40 mesh, 0.08–0.16 mm) in a 100 × 8 mm O.D. tubing was divided into bed A (400 mg) and bed B (200 mg) by using glass wool plugs and polyurethane spacers. The unused ORBO tubes were flame-sealed at both ends. Before use, the tubes were prepared by cutting both ends off using a tube-cutter (Supelco) and smoothed with a file.

2.2. Headspace autosampler and gas chromatograph

A Tekmar (Cincinnati, OH, USA) 7000 static headspace autosampler connected in tandem with a HP 5890 GC (Hewlett-Packard, Fresno, CA, USA) was used for the sample introduction in all the headspace analyses. Manual injection on the GC system was performed when an aliquot of the CS_2 extract was analyzed.

The GC carrier gas (helium for both electron-capture and nitrogen–phosphorus detectors) was split into two flows before entering the headspace autosampler: a carrier flow through a 6-port valve, the heated oven section in the headspace autosampler, the transfer line between headspace autosampler and GC system, and then into the GC column; and a pressurization flow through the lines, sample loop and stationary needle. While in operation, headspace vials containing samples were heated, mixed and equilibrated at a preset temperature for a programmed period of time, and then raised onto the stationary needle, puncturing the septum. Pressurization gas filled the vial via the side pore on the needle, and the original static pressure and the added pressure together drove a fraction of the headspace atmosphere in the vial through the needle and the line into the sample loop. The

6-port valve was then switched and the sample in the sample loop was swept into the GC column by the carrier gas. The concentration of the analyte in the headspace determines the amount of analyte to be delivered to the GC system and therefore the signal output from each injection, and the equilibration of the analyte among the three phases, i.e., headspace, solvent and solid phases, determines the precision of the measurement.

A capillary column (RTX 624, 25 m × 0.25 mm, 1.4 μm; Restek, Bellefonte, PA, USA) was used for the analysis of both 1,3-DCP isomers and MITC. GC conditions used for 1,3-DCP isomers were: electron-capture detector; 1.7 ml min^{-1} column flow-rate; 130°C isothermal oven temperature; 230°C injection port temperature; and 270°C detector temperature. GC conditions used for MITC were: nitrogen–phosphorus detector; 1.7 ml min^{-1} column flow-rate; 170°C isothermal oven temperature; 230°C injection port temperature; and 270°C detector temperature. (Z)-1,3-DCP, (E)-1,3-DCP and MITC were eluted approximately at 3.6, 3.8 and 3.1 min when manual injections were used. A 0.15-min delay was observed for all the retention times when the injections were made from the headspace autosampler.

2.3. Optimization of parameters on headspace autosampler

Many factors contribute to the partition and equilibration of an analyte in a closed headspace vial, among which sample vial equilibrating temperature and time, and the amount of solvent present in the vial, are the most important. Optimization of these three parameters were made by changing one parameter step-wise while maintaining the other two parameters unchanged. All the other parameters other than these three were kept consistent as below in all the optimization processes: 9-ml headspace vial (Tekmar); benzyl alcohol as the solvent; PTFE-faced silicone septa and aluminum seals (Tekmar); 2.0-ml sample loop; 0.5-min mixing time at power level 2; 0.1-min mixing equilibrating time;

12 p.s.i. (1 p.s.i. = 6894.76 Pa) pressurization pressure; 0.25-min pressurization time and 0.1-min stabilizing time; 0.25-min sample loop fill time; 0.1-min sample loop equilibrating time; and 0.5-min sample injecting time. Benzyl alcohol was chosen as the solvent primarily due to its very high boiling point (205.3°C). Canela and Muehleisen [23] used benzyl alcohol and water as extracting solvents in analyzing organic volatiles adsorbed on charcoal by a manual headspace-GC method.

A 20-μg amount of 1,3-DCP (Z)- or (E)-isomer, or MITC in 2 μl methanol was added into the A bed of prepared ORBO-32 or ORBO-306 tubes using a gas-tight syringe, and air was drawn through the tubes at 100 ml min^{-1} for 1 h to simulate samples taken off from an active air sampling device. The charcoal in the spiked ORBO tubes was then emptied into the headspace vials, and glass wool and polyurethane foams were carefully removed.

For the optimization of equilibrating temperature, 1.0 ml benzyl alcohol was added and the sample vials were sealed immediately with septa-lined aluminum caps using a hand crimper. The vials were equilibrated in the headspace autosampler for 5 min at 100, 110, 120, 130, 140, 150, 160, 180 or 200°C. Higher temperatures were not tested since the maximum temperature allowed in the headspace autosampler was 200°C. The optimal temperature was selected based on the GC signal output (in peak area) from each measurement. Two duplicates were used for each temperature level.

Using the optimal equilibrating temperature and 1.0 ml benzyl alcohol, the spiked standards were heated for 1, 2, 3, 4, 5, 6, 8, 10 or 20 min in the headspace autosampler, and the optimal equilibrating time was then selected based on the produced GC signal output from each injection. Two duplicates were included for each time step.

For the optimization of the solvent volume, 0.5, 1.0, 2.0 and 3.0 ml benzyl alcohol were added into the vials containing the spiked standards, and analysis was then completed using the optimal equilibrating temperature and time. The optimal solvent volume was then decided based on the produced signal output of each GC

analysis. Two duplicates were used for each different solvent volume.

2.4. Sensitivity and precision of analysis

The sensitivity and precision of analysis were measured for each compound–ORBO tube combination using the respective optimized headspace methods, and comparisons were made to the analysis using the conventional CS_2 extraction method. Various known amounts (0.1 to 100 μg) of 1,3-DCP (Z)- or (E)-isomer or MITC in methanol were spiked on ORBO-32 or ORBO-306 tubes. The spiked ORBO tubes were exposed to air flux and the charcoal content was transferred into headspace vials as described above. The optimized headspace methods or the CS_2 extraction method were then used to analyze the spiked samples. When the CS_2 method was used, the charcoal was extracted with 4.0 ml CS_2 in sealed headspace vials for 60 min with periodical shaking, and 5 μl of the extract were injected manually into the GC system using a gas-tight syringe (Hamilton, Reno, NV, USA). Two duplicates were used for each concentration level, and the averaged response in peak area from each concentration was plotted against the amount of chemical spiked to generate the calibration curves. The MDL was estimated from the lower end of the calibration curves by assuming the detectable peak area to be three times the background noise. Sensitivity of analysis for each method was also evaluated by comparing the slopes of the linearized calibration curves.

The precision of each method was measured as the standard deviation of multiple analyses using the same method. The mixture of the (Z)- and (E)-isomers of 1,3-DCP, or MITC, was spiked onto ORBO-32 or ORBO-306 tubes at rates equivalent to 4 and 20 μg per tube for (Z)-1,3-DCP and MITC, or 1.52 and 7.61 μg per tube for (E)-1,3-DCP, and the spiked tubes were then analyzed using the respective optimized headspace methods or the CS_2 method. Four replicates were used for each method and concentration level. The calibration curves generated above were used for the quantitation of each measurement.

3. Results and discussion

3.1. Optimization of headspace analysis conditions

When a sealed vial containing charcoal sample is heated in one of the platens in the headspace autosampler, some of the analyte adsorbed on the surfaces of charcoal particles was desorbed by the solvent and redistributed among the vapor, solvent and solid phases. The relationships among the concentrations and these three phases can be described as in Eqs. 1–3, assuming the total distribution of the analyte among the three phases equals P:

$$C_1/C_a = K_H \qquad (1)$$

$$C_s/C_1 = K_d \qquad (2)$$

$$C_a V_a + C_1 V_1 + C_s M_s = P \qquad (3)$$

where C_a, C_1 and C_s are the concentrations of analyte in the headspace, solvent and solid phase, respectively; V_a, V_1 and M_s are the volumes of headspace and solvent, and the mass of charcoal, respectively; K_H is the partition coefficient between the headspace and solvent phases, or the Henry's constant; and K_d is the partition coefficient between the solvent and solid phases, or the adsorption coefficient. Rearranging the equations will result in the expression for the concentration of analyte in the headspace phase:

$$C_a = \frac{P}{V_a + K_H V_1 + K_H K_d M_s} \qquad (4)$$

Obviously, reducing the headspace volume V_a, volume of solvent V_1 or mass of charcoal M_s, or decreasing K_H or K_d will all lead to the increase of C_a and therefore maximize the amount of analyte entering the GC system.

Two sizes of headspace vials, 21 and 9 ml, were available for the Tekmar 7000 headspace autosampler. To reduce the headspace volume, the smaller version of the headspace vials (9 ml) was chosen in this study. Mass of charcoal is usually decided based on the trapping efficiency

and the initial concentration in the air. Large ORBO tubes are necessary when large sampling volume and high flow-rate are required. Solvent volume cannot be indefinitely small since the amount of solvent should be sufficient to bring all the charcoal particles into contact with the solvent to obtain maximum desorption.

K_H and K_d are functions of the analyte as well as the chosen solvent and charcoal types. Once the types of solvent and charcoal are chosen, K_H and K_d can be influenced by the equilibrating temperature in the closed vial as well as the equilibrating time of the vial. Increases of temperature drive the analyte from solvent phase into the vapor phase, and accelerate the desorption of the analyte from the solid surface into the solvent phase. However, a high temperature may cause the decomposition of the analyte in the presence of solvent and charcoal adsorbent and therefore, as a net result, C_a may decrease. Using a longer equilibrating time may also lead to increased decomposition and a smaller C_a. However, if the equilibrating time is too short, equilibrium of the analyte among the three phases is not achieved, which may affect the reproducibility of the analysis.

Signal output generated from the analysis of ORBO tubes spiked with 20 μg 1,3-DCP (Z)- or (E)-isomer or MITC revealed a close dependence of response on the equilibrating temperature (Fig. 1). Equilibrating temperature had different effects on the detection response for different ORBO tubes. On petroleum-based ORBO-306 charcoal tubes, using the same equilibrating time, the produced response increased steadily with increases of equilibrating temperature from 100 to 200°C for both 1,3-DCP isomers and MITC (Fig. 1). The increases were almost linear over the range of 100 to 200°C for all the three compounds, and at 200°C, the signal output was enhanced 5.3, 6.0 and 12.5 times compared to that at 110°C for (Z)-1,3-DCP, (E)-1,3-DCP and MITC, respectively. The selected optimum equilibrating temperature for 1,3-DCP isomers and MITC on ORBO-306 were 190 and 180°C, which were slightly below the maximum temperature allowed on the instrument and the boiling point of benzyl alcohol. On coconut-
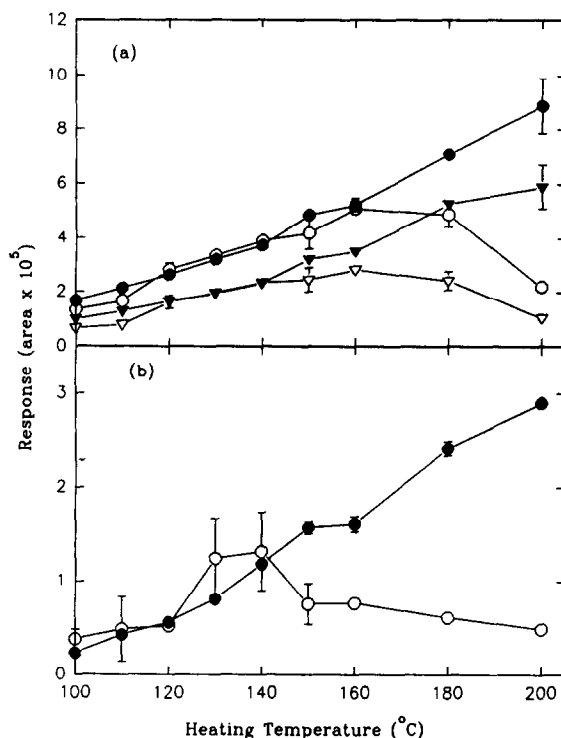

Fig. 1. Effect of equilibrating temperature in the headspace autosampler on response of analysis. (a) 1,3-DCP: equilibrating time 5.0 min and solvent volume 1.0 ml; $\bigcirc$, $\bullet = (Z)$-isomer; $\triangledown$, $\blacktriangledown = (E)$-isomer; $\bigcirc$, $\triangledown = $ ORBO-32; $\bullet$, $\blacktriangledown = $ ORBO-306. (b) MITC: equilibrating time 5.0 min and solvent volume 1.0 ml; $\bigcirc = $ ORBO-32; $\bullet = $ ORBO-306.

based ORBO-32 charcoal tubes, however, the produced response first increased and then decreased rapidly with the increase of equilibrating temperature, and therefore an optimal temperature point existed for all the three compounds. When a 5-min equilibrating time was used, the determined optimal equilibrating temperature on ORBO-32 tubes was approximately 160°C for both (Z)- and (E)-isomers of 1,3-DCP, and 140°C for MITC. More variation was consistently observed on ORBO-32 tubes, particularly for MITC (Fig. 1b). It could be concluded that coconut charcoal had higher reactivity towards these compounds at high temperature, which might be attributed to the catalytic contents such as bases in the plant-based charcoal. Poor storage stability was reported for 1,2-dichloropropane and 1,2-dibromo-3-chloropropane on

coconut-based charcoal at room temperature [21,24]. A daily loss of 7% for a 10-μg spike of 1,2-dibromo-3-chloropropane on coconut-based charcoal at 24°C was observed [24]. Alkyl iso-cyanates are known for their additive reactions with aliphatic alcohols to form thiocarbamates, and the reaction is catalyzed in the presence of alkoxide anions [25]. The catalytic ability of coconut-based charcoal at elevated temperatures and the potential reaction of MITC with benzyl alcohol may be combined to explain the ob-served enhanced decomposition of MITC on ORBO-32 charcoal at high temperatures. When coconut-based charcoal tubes have to be used, alternative high-boiling solvents, such as tetrahy-dronaphthalene, benzyl esters, or polyethers, should be tried to substitute benzyl alcohol for the extracting agent. The effect of benzyl al-cohol–MITC reaction on petroleum-based char-coal was not significant, since good reproducibil-ity and linear increase of sensitivity with increas-ing equilibrating temperature were clearly ob-served (Fig. 1b). Petroleum-based charcoal tubes are therefore recommended over coconut-based tubes for MITC sampling if headspace analysis is to be performed.

At the same equilibrating temperature, the signal output produced from the same amount of the (E)-isomer of 1,3-DCP was consistently lower than that from the (Z)-isomer (Fig. 1a). This difference could be explained by the higher boiling point (112°C) and smaller vapor pressure (34 mmHg at 25°C; 1 mmHg = 133.322 Pa) of the (E)-isomer than the (Z)-isomer, which had a boiling point of 104.3°C and a vapor pressure of 43 mmHg at 25°C.

The equilibrating time at the selected optimal temperatures was varied from 1 to 20 min, and the signal output of each analysis was correlated to the equilibrating time (Fig. 2). When the ORBO-32 and -306 tubes spiked with 1,3-DCP isomers were heated at 160 and 190°C, respec-tively, the response increased within the first 4–5 min, and then gradually decreased with the increase of equilibrating time (Fig. 2a). Similar dependence of the detection response on the equilibrating time was observed for both the (Z)- and (E)-isomers of 1,3-DCP on both ORBO
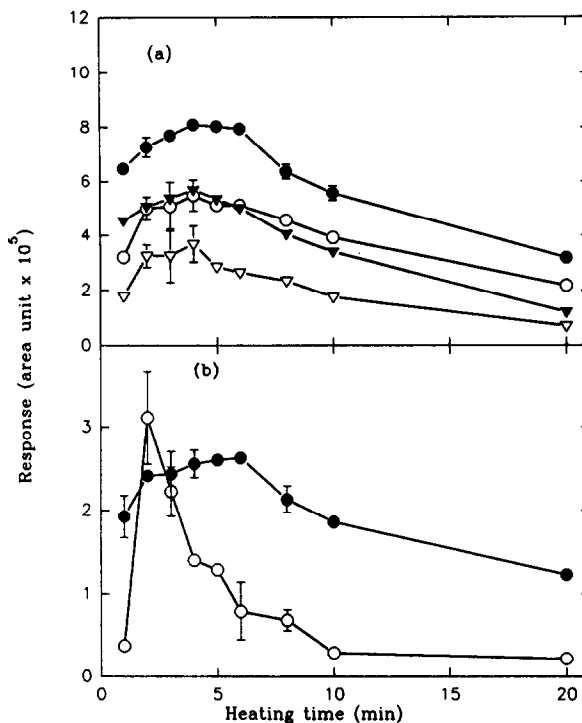

Fig. 2. Effect of equilibrating time in the headspace auto-sampler on response of analysis. (a) 1,3-DCP: equilibrating temperature 160°C for ORBO-32 (O, ∇) and 190°C for ORBO-306 (●, ▼) tubes, and solvent volume 1.0 ml; O, ● = (Z)-isomer; ∇, ▼ = (E)-isomer. (b) MITC: equilibrating temperature 140°C for ORBO-32 (O) and 180°C for ORBO-306 (●) tubes, and solvent volume 1.0 ml.

tubes. However, more significant variations were observed on ORBO-32 tubes when the equili-brating time was less than 5 min, indicating equilibrium of the distribution of 1,3-DCP among the phases was not well achieved within such a short period of time. A 5-min period was therefore selected as the optimal time for the equilibrating temperatures used for both isomers of 1,3-DCP on both ORBO tubes. The signal output reached the maximum at 2 min for MITC on ORBO-32 tubes when 140°C was used as the equilibrating temperature, but decreased rapidly with further increases of time (Fig. 2b). A 3-min period was therefore determined as the optimal equilibrating time for MITC on ORBO-32 tubes. On petroleum-based ORBO-306 tubes, the re-sponse almost remained constant from 2–6 min
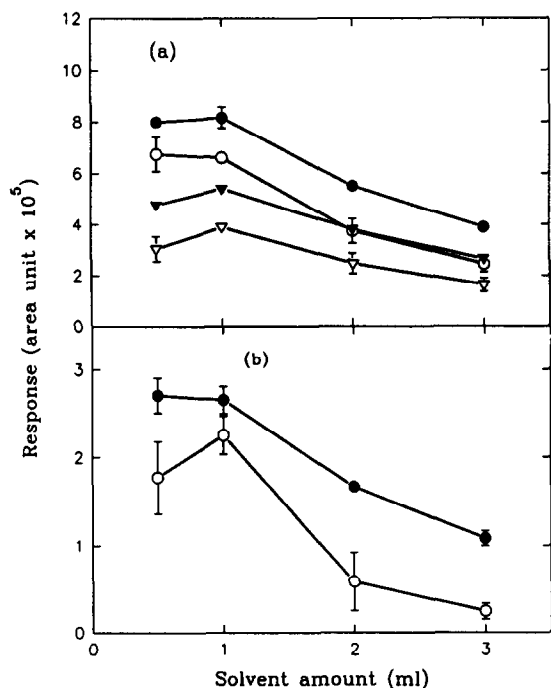
Fig. 3. Effect of solvent volume in the headspace vials on response of analysis under the optimum equilibrating temperature and time. (a) 1,3-DCP; O, ● = (Z)-isomer; ▽, ▼ = (E)-isomer; O, ▽ = ORBO-32; ●, ▼ = ORBO-306. (b) MITC; O = ORBO-32; ● = ORBO-306.

and then decreased gradually with further increases of the equilibrating time, and 5 min was decided as the optimal time. MITC was apparently more resistant to longer equilibrating time on ORBO-306 tubes than on ORBO-32 tubes. Longer equilibrating time may affect the response of analysis by increasing the decomposition of the analyte in the heated headspace vials.

Using the optimal equilibrating temperatures

and times, the effect of solvent volume on the production of response from each analysis was determined (Fig. 3). The signal output was approximately the same when 0.5 or 1.0 ml benzyl alcohol was added into the headspace vials, but decreased proportionally when the solvent volume further increased to 2.0 and 3.0 ml. However, more variations were noticed for most of the compound–charcoal tube combinations when 0.5 ml solvent volume was used, which may be attributed to the possibility that not all of the charcoal particles were in contact with the solvent when the amount of solvent was so small. A 1-ml volume was therefore determined as the optimal amount of solvent for all the headspace methods. Effect of the amount of solvent on the detection sensitivity was obviously due to that more solvent increased the partition of the analyte into the solvent phase and concurrently decreased its concentration in the vapor phase.

The parameters of the optimized headspace methods for 1,3-DCP isomers and MITC on ORBO-32 and -306 tubes were summarized in Table 1. It is obvious that different optimal parameters exist for different compound–charcoal tube combination, and therefore different conditions should be used to achieve the maximum sensitivity of analysis.

3.2. Sensitivity and precision of measurements

Calibration curves between peak area and amount of compound spiked on ORBO tubes were constructed for each optimized headspace method as well as for the CS_2 method on

Table 1
Optimized parameters for headspace analysis of 1,3-DCP and MITC on ORBO-32 and -306 charcoal tubes

Parameter	1,3-DCP		MITC	
	ORBO-32	ORBO-306	ORBO-32	ORBO-306
Equilibrating temperature(°C)	160	190	140	180
Equilibrating time (min)	5	5	3	5
Solvent volume (ml) (benzyl alcohol)	1.0	1.0	1.0	1.0

different ORBO tubes (Fig. 4). Good linearity was noticed over the concentration range of 0.1–100.0 μg per tube for all the methods ($r^2 > 0.99$ in all situations). All the optimized headspace methods were significantly superior to the solvent-phase analysis method on the sensitivity of measurement. The calculated slopes of the linearized calibration curves on ORBO-32 and -306 tubes obtained with the optimized headspace methods were 12 and 32 times of those obtained with the CS_2 method for (Z)-1,3-DCP, 8 and 21 times for (E)-1,3-DCP, and 12 and 14 times for MITC, respectively. Petroleum-based

ORBO-306 tubes constantly gave better sensitivity than coconut-based ORBO-32 tubes for all the three compounds (Fig. 4). A large dilution factor may be used to explain the relatively low sensitivity for the CS_2 method. With the CS_2 method, since only 5 μl of the 4 ml extract were eventually injected into the GC system, the dilution was 800 times even when a complete desorption was assumed.

The estimated MDL was at least one order of magnitude smaller for the optimized headspace methods than the CS_2 method for all the compound–charcoal tube combinations (Table 2). Assuming 40 l of air are collected using the ORBO-32 or -306 tubes, the estimated minimum detectable concentrations of the analyte in air would be 0.01 and 0.005 μg m^{-3} for (Z)-1,3-DCP, 0.03 and 0.01 μg m^{-3} for (E)-1,3-DCP, and 0.05 and 0.08 μg m^{-3} for MITC, respectively, which were significantly improved from the MDL of 0.2 and 1.0 μg m^{-3} reported for 1,3-DCP and MITC on petroleum-based charcoal tubes [21].

Measurements of replicated spiked samples using the above calibration curves showed that except for MITC on ORBO-32 tubes, analysis with the optimized headspace methods was highly reproducible and the precision was approximately the same as using the CS_2 method (Table 2). The standard deviation calculated from four replicate analyses was less than 10% for all the measurements made by using the headspace methods except for the MITC–ORBO-32 combination. Analysis of ORBO-32 tubes spiked with MITC was low in reproducibility, which may be attributed to the poor stability of this compound on the coconut-based charcoal at the selected equilibrating temperature. It is important to point out that the optimized headspace methods, due to the complete automation, are less labor-intensive and high in sample throughput. For the GC conditions used in this study, one analysis was completed within 6 min, and up to 200 charcoal samples may be analyzed on a 24-h basis. The consumption of solvent is significantly reduced. Since CS_2 is highly flammable and toxic, the safety of operation is also improved when the headspace methods are used.
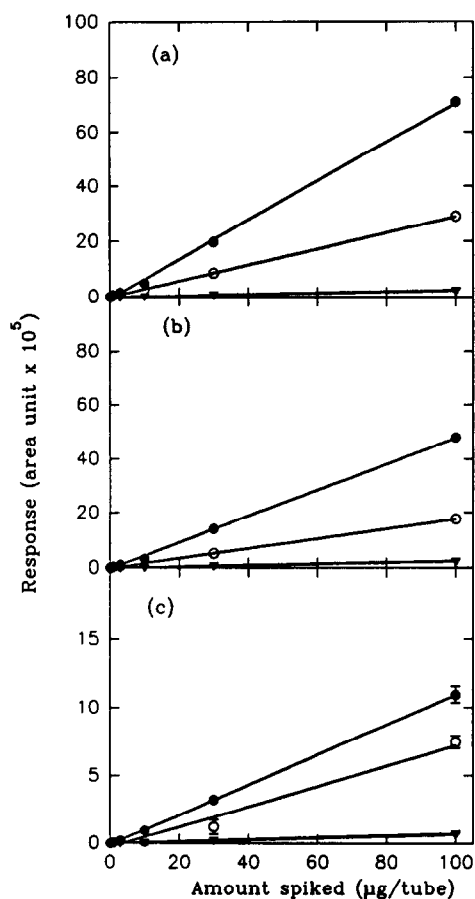

Fig. 4. Calibration curves of the optimized headspace methods (HS) and the solvent extraction method with CS_2 (CS_2). (a) (Z)-1,3-DCP; (b) (E)-1,3-DCP; (c) MITC. O = ORBO-32, HS; ∇ = ORBO-32, CS_2; ● = ORBO-306, HS; ▼ = ORBO-306, CS_2.

Table 2
MDL ± S.D. of analysis by different methods

	Amount spiked (μg per tube)	ORBO-32		ORBO-306	
		HS method[a]	CS$_2$ method[b]	HS method	CS$_2$ method
MDL (ng per tube)					
MITC		3.0	30	2.0	20
(Z)-Isomer		0.5	7.7	0.2	10.8
(E)-Isomer		1.1	7.3	0.5	10.6
Recovery (μg per tube; n = 4)					
MITC	4.0	3.16 ± 1.29	2.89 ± 0.26	4.20 ± 0.44	3.92 ± 0.17
	20.0	16.20 ± 7.68	18.43 ± 2.04	20.48 ± 1.58	19.28 ± 0.40
(Z)-1,3-DCP	4.0	4.07 ± 0.07	3.71 ± 0.33	3.78 ± 0.22	4.20 ± 0.32
	20.0	19.01 ± 0.22	19.77 ± 0.55	20.15 ± 0.54	21.09 ± 0.60
(E)-1,3-DCP	1.52	1.49 ± 0.07	1.45 ± 0.14	1.48 ± 0.08	1.61 ± 0.12
	7.61	7.14 ± 0.19	7.61 ± 0.22	7.79 ± 0.25	8.04 ± 0.25

[a]HS method: the optimized headspace methods.
[b]CS$_2$ method: analysis of solvent extract after extraction with CS$_2$.

4. Conclusions

Headspace techniques are applicable for the analysis of 1,3-DCP isomers and MITC on charcoal sampling tubes, and more than one order of magnitude higher sensitivity than the standard solvent-phase analysis approach was achieved under optimum conditions. Equilibrating temperature and time, and the amount of extracting solvent, could all be adjusted to maximize the signal output of each GC analysis. All the three compounds were less stable on coconut-based charcoal at high temperature, and a lower equilibrating temperature and a short equilibrating time therefore had to be used. However, better sensitivity and reproducibility were observed for all the three compounds on petroleum-based charcoal tubes. The estimated minimum detection limits for the (Z)- and (E)-isomer of 1,3-DCP and MITC were 0.2, 0.5 and 2.0 ng per tube on the petroleum-based ORBO-306 tubes, and 0.5, 1.1 and 3.0 ng per tube on coconut-based ORBO-32 tubes, respectively. Assuming 40 l of air are sampled, the corresponding MDLs in concentration were 0.005, 0.01 and 0.05 μg m^{-3} on ORBO-306 tubes, and 0.01, 0.03 and 0.08 μg m^{-3} on ORBO-32 tubes, respectively.

Precision of measurement was comparable to the CS$_2$ method except for MITC on ORBO-32 tubes. Sample output and safety of operation were also significantly improved compared to the conventional solvent-phase analysis using CS$_2$. Applications of the headspace method to other volatile compounds, including some common pollutants of industrial origin, are worth further exploration.

References

[1] R.S.H. Yang, *Residue Rev.*, 97 (1986) 19.
[2] M. Ottnad, N.A. Jenny and C.H. Röder, in G. Zweig and J. Sherma (Editors), *Analytical Methods for Pesticides and Plant Regulators*, Vol. 10, Academic Press, New York, 1978, pp. 563–573.
[3] J.H. Smelt and M. Leistra, *Pestic. Sci.*, 5 (1974) 401.
[4] M. Basile, N. Senesi and F. Lamberti, *Agric., Ecosyst. Environ.*, 17 (1986) 269.
[5] S.A. Ness, in S.A. Ness (Editor), *Air Monitoring for Toxic Substances: an Integrated Approach*, Van Nostrand Reinhold, New York, 1991, pp. 51–92.
[6] E.V. Kring, G.R. Ansul, T.J. Henry, J.A. Morello, S.W. Dixon, J.F. Vasta and R.E. Hemingway, *Am. Ind. Hyg. Assoc. J.*, 45 (1984) 250.
[7] R.H. Brown and C.J. Purnell, *J. Chromatogr.*, 178 (1979) 79.

[8] W.T. Jr. Winberry, N.Y. Murphy and R.M. Riggan, in W.T. Winberry, Jr., N.Y. Murphy and R.M. Riggan, (Editors), *Methods for Determination of Toxic Organic Compounds in Air; EPA Methods, Method T010*, Noyes Data Corp., Park Ridge, NJ, 1990, pp. 257–293.

[9] J.B. Mann, J.J. Freal, H.F. Enos and J.X. Danauskas, *J. Environ. Sci. Health*, B15 (1980) 507.

[10] L.G.M. Th. Tuinstra, W.A. Traag and A.H. Roos, *J. High Resolut. Chromatogr. Chromatgr. Commun.*, 11 (1988) 106.

[11] B.D. Page and R.J. Avon, *J. Assoc. Off. Anal. Chem.*, 72 (1989) 815.

[12] K.N.T. Norman, *Pestic. Sci.*, 33 (1991) 23.

[13] R. Otson and D.T. Williams, *Anal. Chem.*, 54 (1982) 942.

[14] Z. Penton, *J. High Resolut. Chromatogr.*, 15 (1992) 834.

[15] P.H. Kiang and R.L. Grob, *J. Environ. Sci. Health*, A21 (1986) 71.

[16] T.C. Voice and B. Kolb, *Environ. Sci. Technol.*, 27 (1993) 709.

[17] D. Jentzsch, J. Krüger, H.G. Lebrecht, G. Dencks and J. Gut, *Z. Anal. Chem.*, 236 (1968) 96.

[18] B. Kolb, *J. Chromatogr.*, 122 (1976) 553.

[19] J.E. Woodrow, M.M. McChesney and J.N. Seiber, *Anal. Chem.*, 60 (1988) 509.

[20] J. Gan, S.R. Yates and W.F. Spencer, *J. Agric. Food Chem.*, submitted for publication.

[21] F. van den Berg, M. Leistra, A.H. Roos and L.G.M. Th. Tuinstra, *Water, Air, Soil Pollut.*, 61 (1992) 385.

[22] A. Collina and P. Maini, *Bull. Environ. Contam. Toxicol.*, 22 (1979) 400.

[23] A.M. Canela and H. Muehleisen, *J. Chromatogr.*, 456 (1988) 241.

[24] W.N. Albrecht, M.R. Hagadone and K. Chenchin, *Bull. Environ. Contam. Toxicol.*, 36 (1986) 629.

[25] W. Walter and K.-D. Bode, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 281.